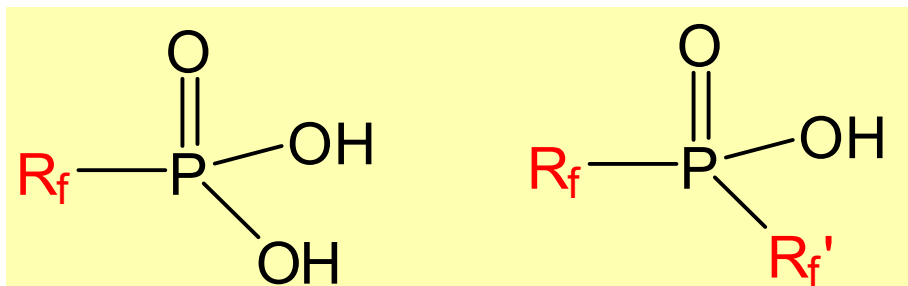


# Fluoroalkyl-phosphonic-acid-based proton conductors



**Stephen Creager (PI) and Darryl DesMarteau  
Clemson University**

and

**Oleg Borodin, Grant Smith, and Gregory Voth  
University of Utah**

Annual DOE Merit Review, Hydrogen Program

Washington DC, June 11, 2008

**FC 18**

# Overview

## Timeline

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

## Budget

- Total project funding
  - DOE \$1,500,000
  - Contractor \$381,000
- Funding for FY 06 and 07
  - \$450,000 rec'd from DOE for work performed between April 2006 and Sept 2007
- Funding for FY08
  - None to date

## Barriers

- Barriers
  - A,B,C; Durability / Cost / Performance.
- Targets
  - Membrane conductivity > 0.07 S/cm at 20 °C and water partial pressure of 1.5 kPa
  - Membrane conductivity > 0.10 S/cm at operating temp (120 °C) and water partial pressure of 1.5 kPa

## 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)

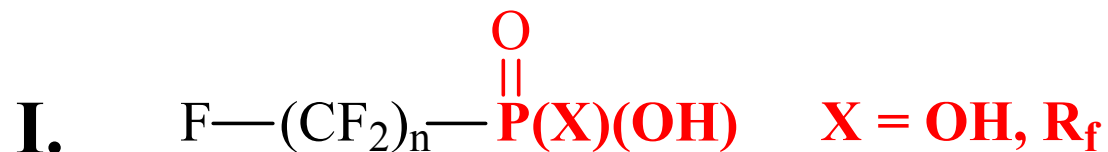
# Objectives / Tasks / Milestones

Specific project objectives	<p>(1) <b><u>Synthesize and characterize new proton-conducting electrolytes</u></b> based on the fluoroalkylphosphonic acid functional group; and</p> <p>(2) <b><u>Perform simulation study</u></b> of structure and proton conduction in fluoroalkylphosphonic acid-based electrolytes.</p>
Year 2 Tasks and Milestones (April 2007 – March 2008)	<ul style="list-style-type: none"><li>• Synthesize and/or purify at least 5 g each of one or more trifluorovinyl-ether (TFVE) fluoroalkylphosphonic acid monomers.</li><li>• Complete development and validation of classical force fields for fluoroalkylphosphonic and fluoroalkyl-bis-phosphinic acids and perform MD simulations of these acids as a function of fluoroalkyl chain length</li><li>• Perform DFT-based Born Oppenheimer Molecular Dynamics (BOMD) simulations of <math>\text{CF}_3\text{PO}_3\text{H}_2</math> and <math>(\text{CF}_3)_2\text{POOH}</math> acids.</li><li>• Complete synthesis of TFVE monomer and development and validation of models and begin MD, CGIS and MPM simulations</li><li>• <b>Milestone: Year 2 (24 months from start): Test the membrane for electrolyte conductivity of at least 0.07 S/cm at 80% RH at ambient temperature and deliver a sample membrane to the Topic 2 contractor for evaluation.</b></li></ul>

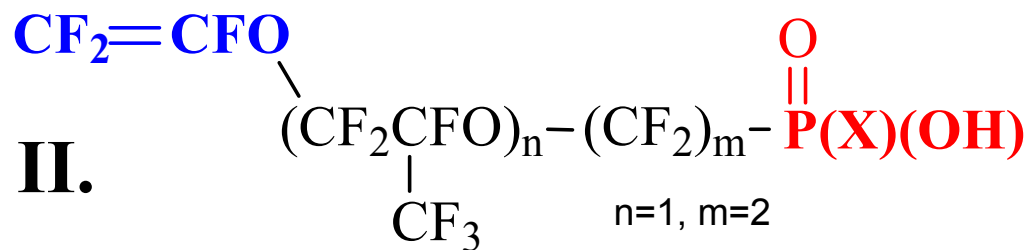
# Approach

<p><b>Task 1.0</b> Synthesize new fluoroalkyl-phosphonic-acid-based electrolytes.</p> <ul style="list-style-type: none"><li>– Small-molecule acid model compounds</li><li>– Trifluorovinylether (TFVE) monomers</li><li>– Copolymers of TFVE monomers with tetrafluoroethylene (TFE) to give ionomer membranes</li></ul>	<p><b>Task 5.0</b> Perform computer simulations of fluoroalkylphosphonic-acid electrolytes.</p> <ul style="list-style-type: none"><li>– Perform classical and DFT-based Born Oppenheimer Molecular Dynamics (BOMD) of various of fluoroalkylphosphonic-acids</li></ul>
<p><b>Task 2.0</b> Characterize new fluoroalkyl-phosphonic-acid-based electrolytes.</p> <ul style="list-style-type: none"><li>– Structure, purity, ion (proton) transport rates (diffusivity, conductivity)</li></ul>	<p><b>Task 6.0</b> Perform computer simulations of fluoroalkylphosphonic acid electrolyte / heterocycle/water mixtures.</p> <ul style="list-style-type: none"><li>– As in Task 5.</li></ul>
<p><b>Task 3.0</b> Demonstrate conductivity of at least 0.07 S/cm at 80% RH at ambient temperature.</p>	<p><b>Task 7.0</b> Project Management and Reporting.</p> <ul style="list-style-type: none"><li>– Deliver membrane(s) to Topic 2 awardee; periodic reports; annual reviews</li></ul>
<p><b>Task 4.0</b> Demonstrate conductivity of at least 0.10 S/cm at 50% RH at 120 °C.</p>	

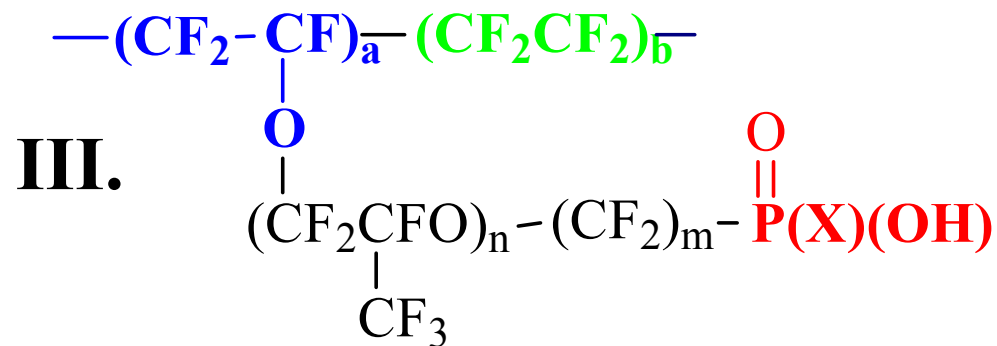
# Electrolyte Structures



Small molecule  
model  
compounds



Trifluorovinylether  
monomers



Fluoroalkylphosphonic  
acid ionomers

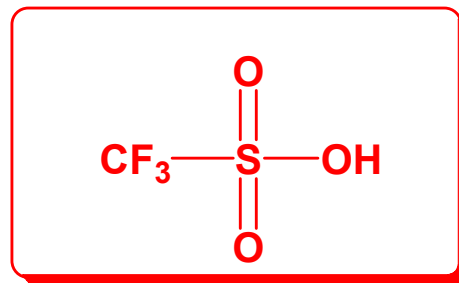
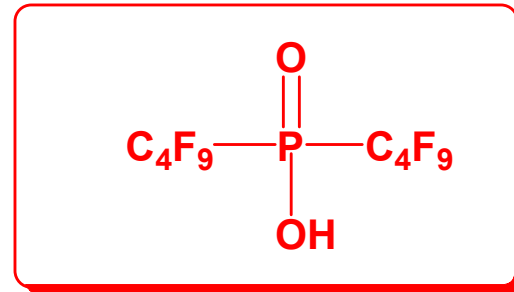
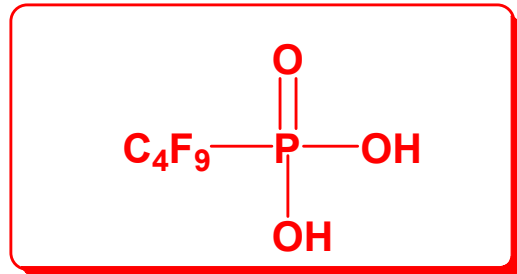
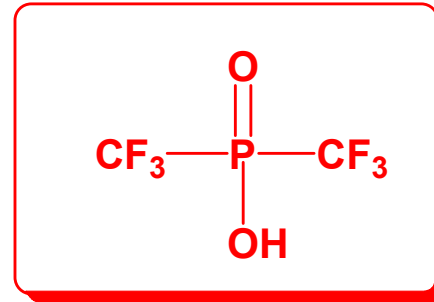
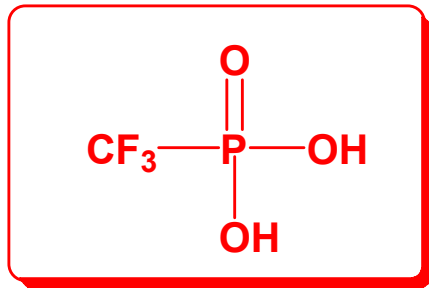
# Technical Accomplishments

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## **FPA electrolytes**

### **1. Synthesis and Characterization**

# Model Compound Structures



**Table 1. Physical Constants for Perfluoroalkylphosphonic and Sulfonic Acids**

	Solid/Liquid at RT	mp, °C	bp, °C (p, mm Hg)	H <sub>2</sub> O solubility
CF <sub>3</sub> PO <sub>3</sub> H <sub>2</sub>	solid	81-82 <sup>a)</sup>	High	soluble
(CF <sub>3</sub> ) <sub>2</sub> PO <sub>2</sub> H	liquid	-	182 (760) <sup>b)</sup>	soluble
CF <sub>3</sub> SO <sub>3</sub> H	liquid	-	160-162 (760) <sup>c)</sup>	soluble, but solid at 1: 1 molar mixture
C <sub>4</sub> F <sub>9</sub> PO <sub>3</sub> H <sub>2</sub>	liquid	-	170-175 (0.5) <sup>d)</sup>	soluble
(C <sub>4</sub> F <sub>9</sub> ) <sub>2</sub> PO <sub>2</sub> H	liquid	-	High	insoluble

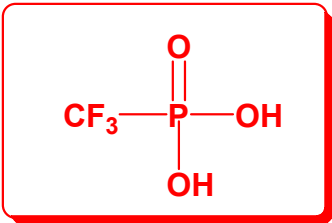
*a) Organometallic and organometalloidal fluorine compounds. X. Trifluoromethyl- phosphonous and -phosphonic acids. Bennett, F. W.; Emeleus, H. J.; Haszeldine, R. N. Univ. Cambridge, UK. Journal of the Chemical Society (1954)*

*b) Emeleus, H. J.; Haszeldine, R. N.; Paul, Ram Chand. Organometallic and organometalloidal fluorine compounds. XII. Bistrifluoromethyl phosphinic acid and related phosphorus oxyacids. Journal of the Chemical Society (1955), 563-74.*

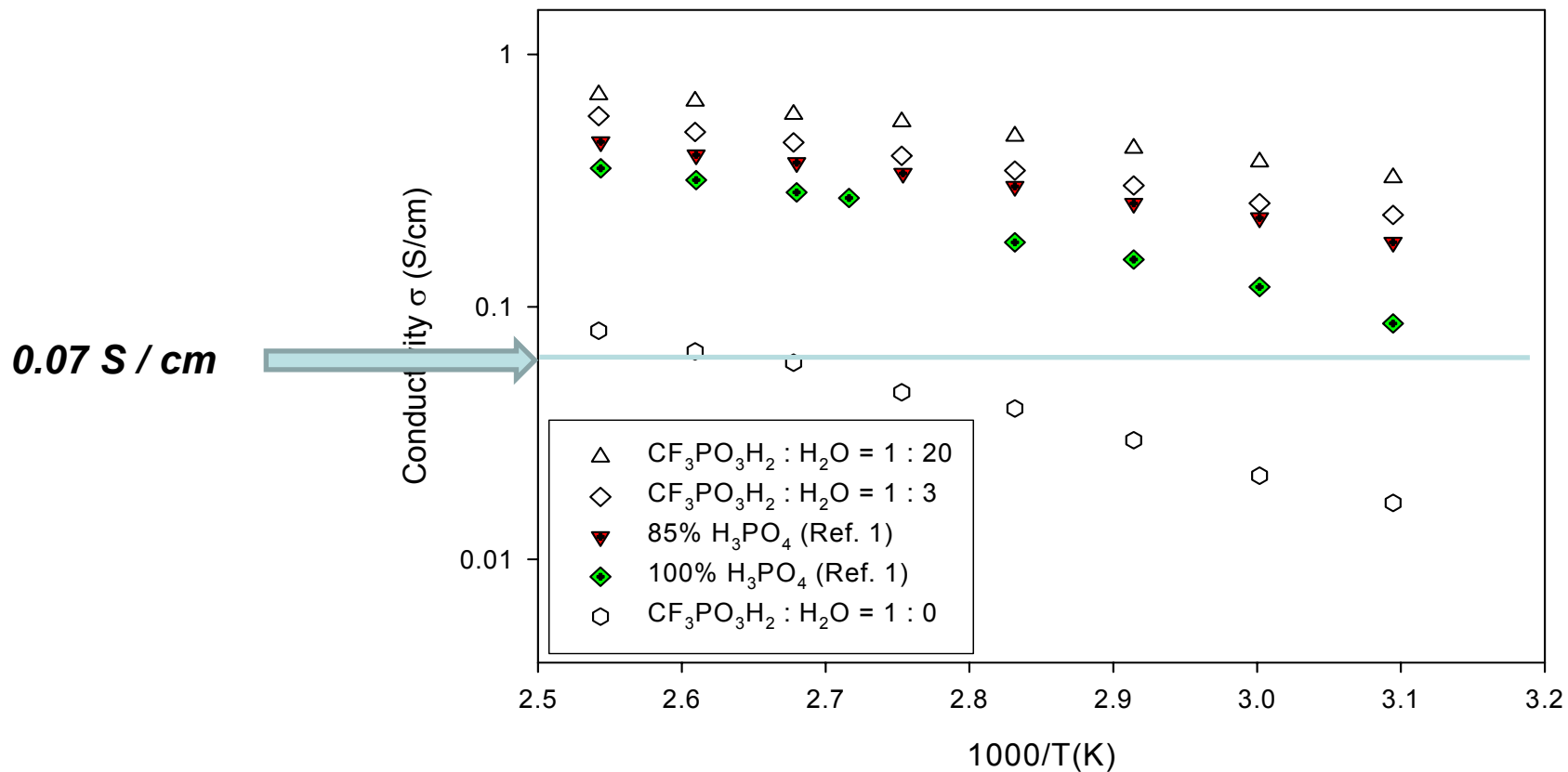
*c) The chemistry of nitrilium salts. Part 1. Acylation of phenols and phenol ethers with nitriles and trifluoromethanesulfonic acid. Booth, Brian L.; Noori, Ghazi F. M. Inst. Sci. Technol., Univ. Manchester, Manchester, UK. Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999) (1980), (12), 2894-900*

*d) Kovaleva, T. V.; Martynyuk, E. G.; Semenii, V. Ya. Perfluoroalkylphosphonic acids and their derivatives. Zhurnal Obshchei Khimii (1989), 59(11), 2512-15.*

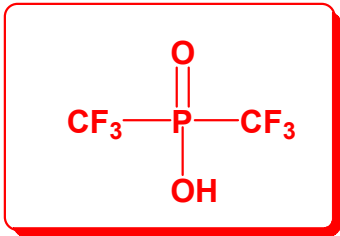




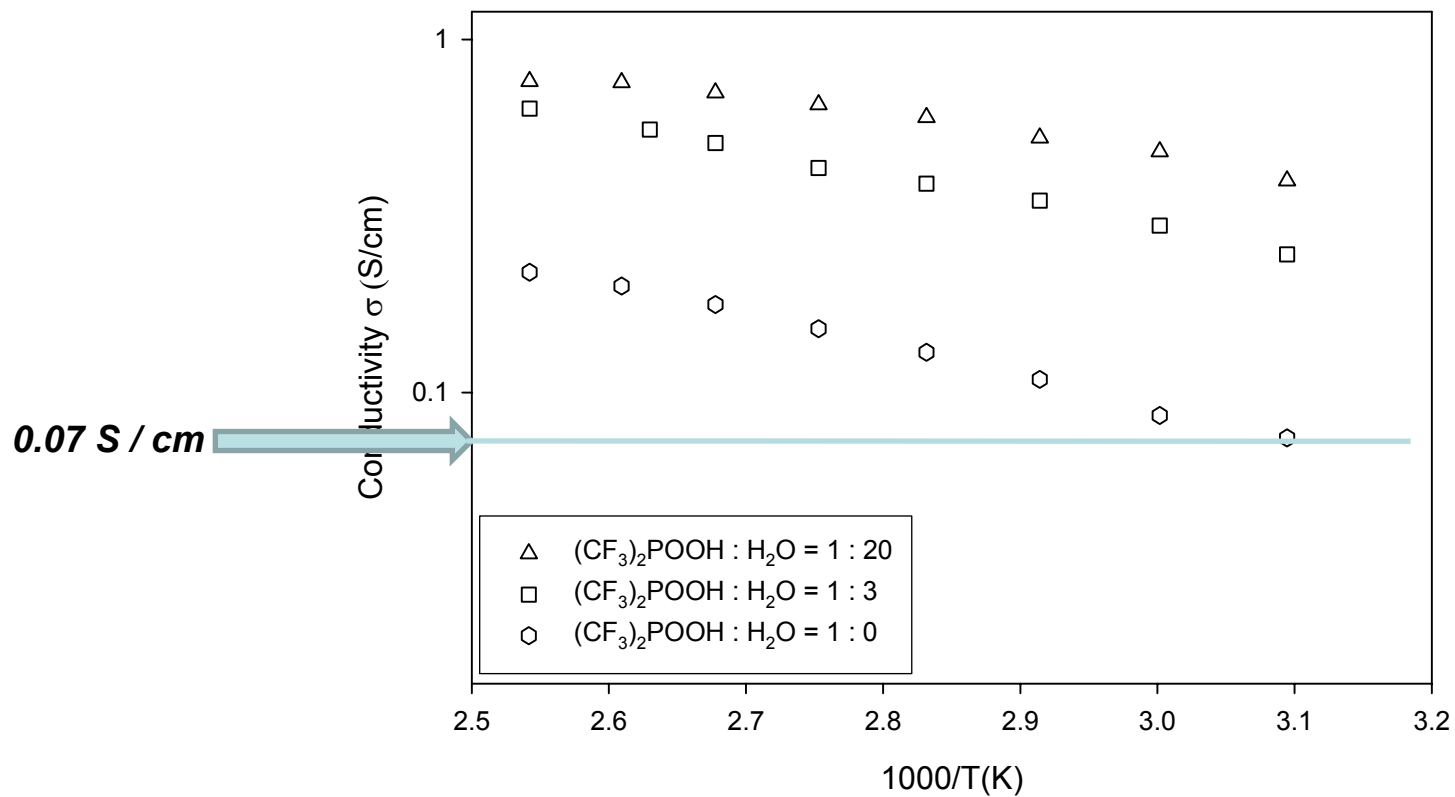
## Conductivity of $\text{CF}_3\text{PO}_3\text{H}_2$ and $\text{H}_3\text{PO}_4$

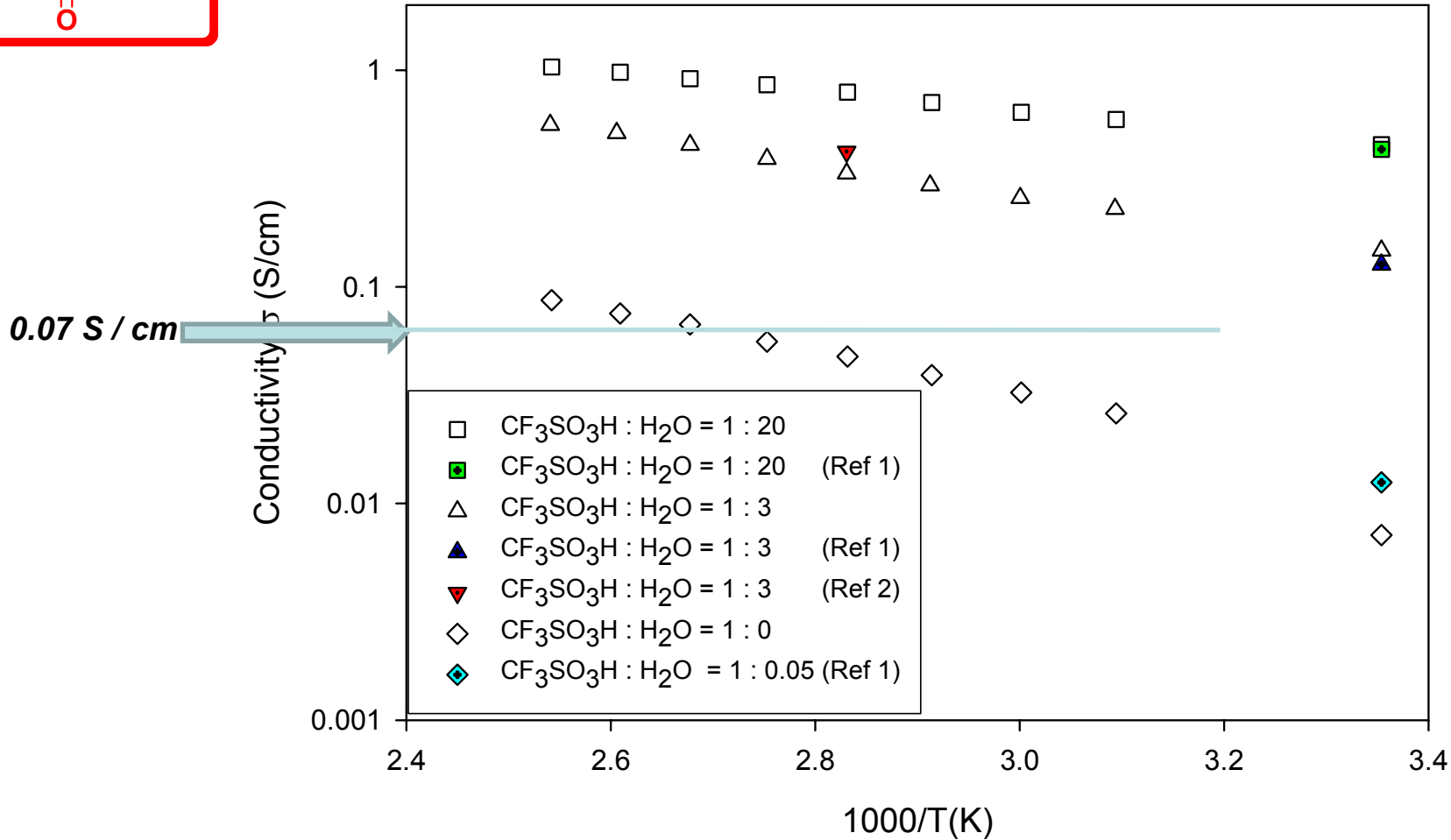
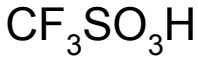
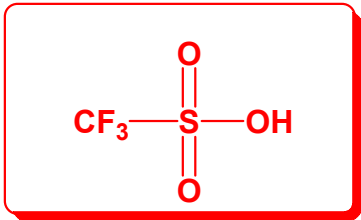


**Ref. 1. Chin and Chang, J Appl Echem 19, 95 (1989)**



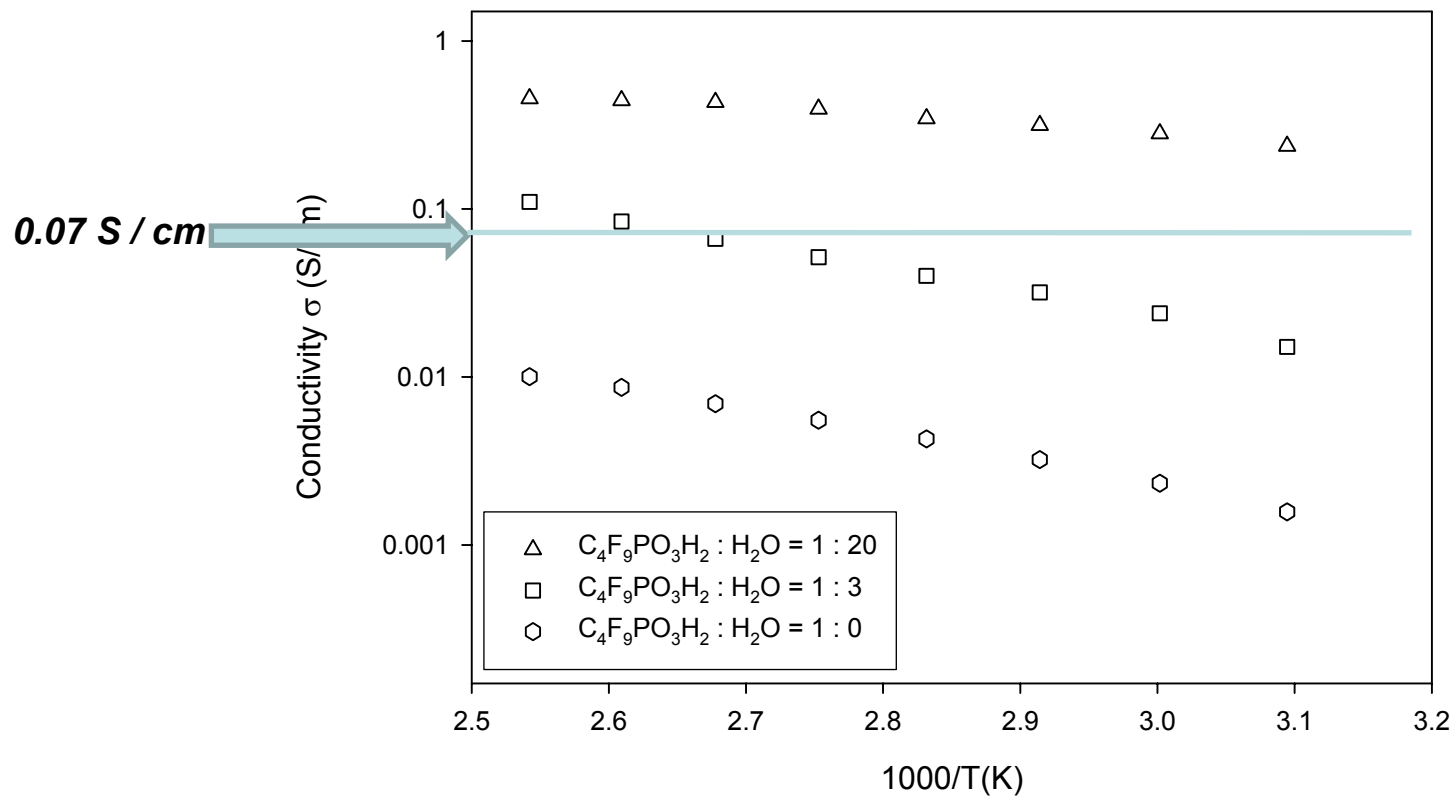
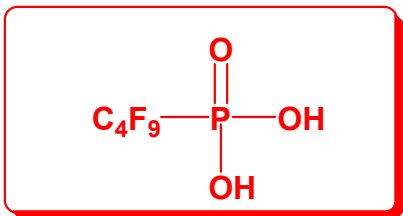
$(CF_3)_2POOH$

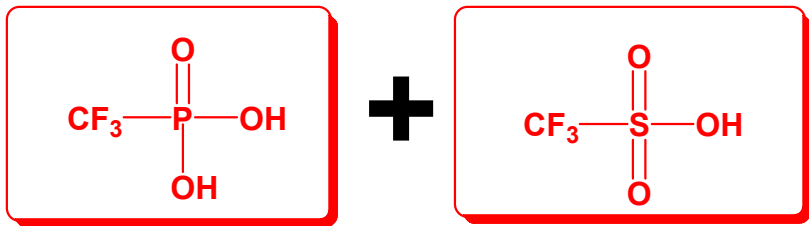




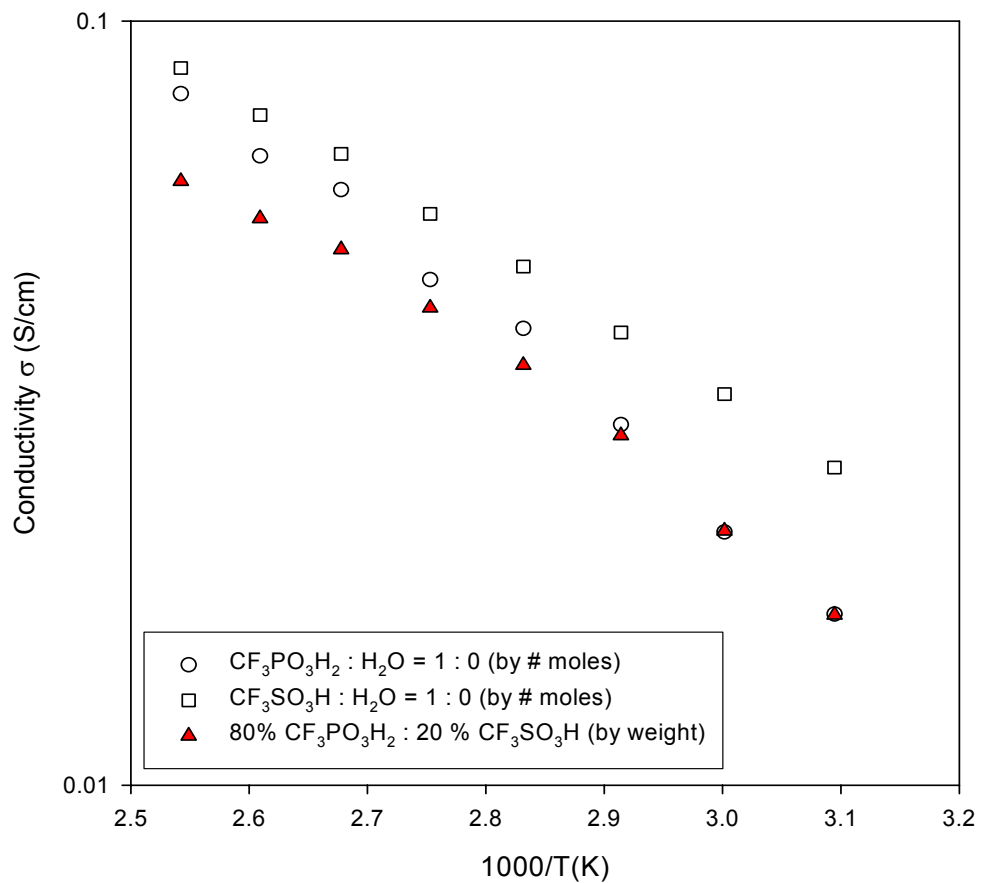
**Ref 1: Canadian Journal of Chemistry (1978), 56(13), 1832-5.**

**Ref 2 : Giner Electrochemical systems LLC. DOE Hydrogen review 2007 pg 8**





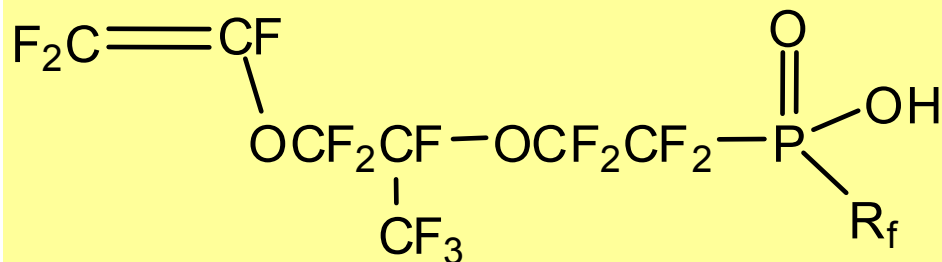
$\text{CF}_3\text{PO}_3\text{H}_2 + \text{CF}_3\text{SO}_3\text{H}$  mixture



# Summary of FPA model compound studies

- Bis(trifluoromethyl)phosphinic acid ( $((\text{CF}_3)_2\text{P}(\text{O})(\text{OH}))$ ) has the highest anhydrous conductivity of all the FPAs tested. It is above that of anhydrous triflic acid and just below that of anhydrous phosphoric acid.
- Addition of small amounts of water causes dramatic increases in conductivity for all acids tested.
- Replacing  $\text{CF}_3$  with  $\text{C}_4\text{F}_9$  in FPAs decreases conductivity especially under very dry conditions.
- Mixtures of superacids (e.g. triflic acid) with FPAs so far do not produce electrolytes having enhanced conductivity. More work is planned in this area, as models for polyfunctional (e.g. terpolymer) ionomers.

# Bis-fluoroalkyl-phosphinic acid ionomers



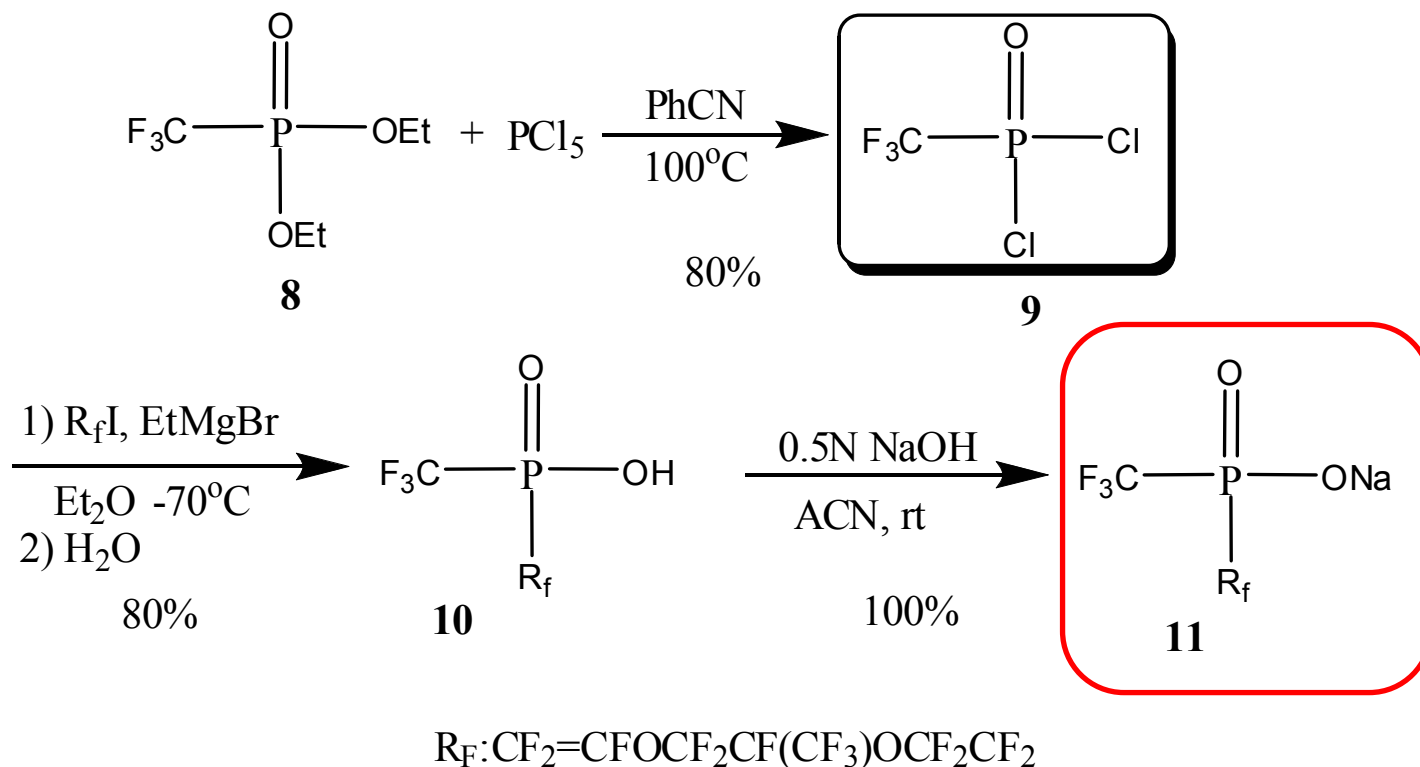
R<sub>f</sub>: C<sub>4</sub>F<sub>9</sub>; CF<sub>3</sub>.

Bis(fluoroalkyl)-phosphinic acid  
Trifluorovinyl ether monomer

- **Monomer 7**, R<sub>f</sub> = C<sub>4</sub>F<sub>9</sub>
- **Monomer 11**, R<sub>f</sub> = CF<sub>3</sub>

- *Should be quite strong acids, proton dissociation is favored*
- *Should be better surfactant in Na<sup>+</sup> form than the mono-fluoroalkylphosphonic acids, therefore more likely to produce good ionomers by emulsion co-polymerization with TFE in water*
- *Should / could promote proton transport by a hopping mechanism (testing is in progress with model compounds)*

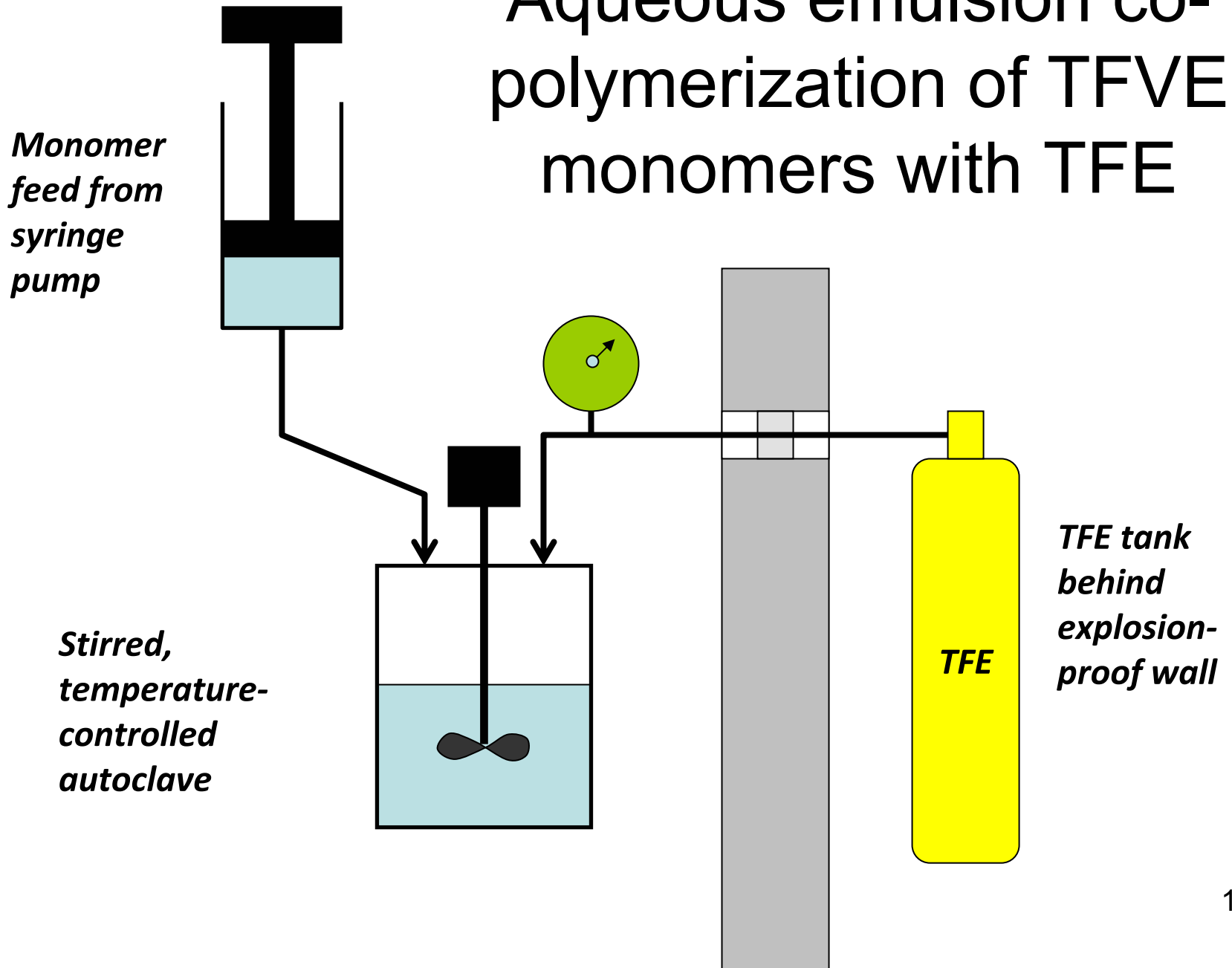
# Synthesis of Monomer 11



> **Monomer 11** was obtained in good yield in multi-gram amounts



# Aqueous emulsion co-polymerization of TFVE monomers with TFE



# Typical conditions for copolymerization of trifluorovinyl ether monomers (**7** and **11**) with TFE

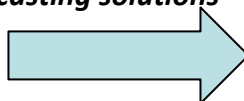
Conditions	<b>P10</b>	<b>P12</b>	<b>P14</b>	<b>P15</b>	<b>P18</b>
Reactor	450 mL	450 mL	450 mL	450 mL	<b>450ml</b>
Monomer	<b>7 (R<sub>f</sub> = C<sub>4</sub>F<sub>9</sub>)</b>	7	7	7	<b>11 (R<sub>f</sub> = CF<sub>3</sub>)</b>
Monomer in the autoclave (g)	4	2	2	2	<b>4</b>
Surfactant C <sub>7</sub> F <sub>15</sub> COONH <sub>4</sub> (g)	2	2	2	2	<b>2</b>
NaH <sub>2</sub> PO <sub>4</sub> (g)	0.77	0.77	0.77	0.77	<b>0.77</b>
Na <sub>2</sub> HPO <sub>4</sub> (g)	1.35	1.35	1.35	1.35	<b>1.35</b>
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (mg)	45	45	45	45	<b>30</b>
Pressure of TFE (psi)	110-105	185-180	110-105	80-75	<b>85-80</b>
Total TFE drop (psi)	24	40	23	20	<b>30</b>
Stirring speed (rpm)	600	600	600	600	<b>600</b>
Reaction temperature (°C)	65	65	65	65	<b>65</b>
H <sub>2</sub> O (ml)	260	260	260	260	<b>220</b>
Head space (ml)	190	190	190	190	<b>230</b>
<b>Polymer weight (g)</b>	<b>3.8</b>	<b>3.95</b>	<b>2.5</b>	<b>2</b>	<b>3</b>
<b>Equiv weight (g / equiv)</b>	<b>750</b>	<b>1300</b>	<b>1000</b>	<b>910</b>	<b>1000</b>
Water uptake, meth 1, 100C	123%	16%	74%	80%	<b>30%</b>
Water content, meth 2, 25C	47%	7%	37%	39%	-

Because of the good solubility of these polymers, membranes were readily formed from casting solutions. As examples, membranes from ionomers **P10** and **P18** are shown below.

**P10**



casting solutions



- Membrane from P10
- Thickness: 64um
- Flexible and tough
- Colorless after boiling in  $\text{HNO}_3$

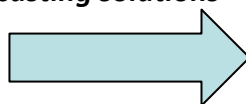
Copolymer from copolymerization  
of  $R_F\text{P}(\text{O})(\text{ONa})\text{C}_4\text{F}_9$  with TFE

**P10-mem**

**P18**



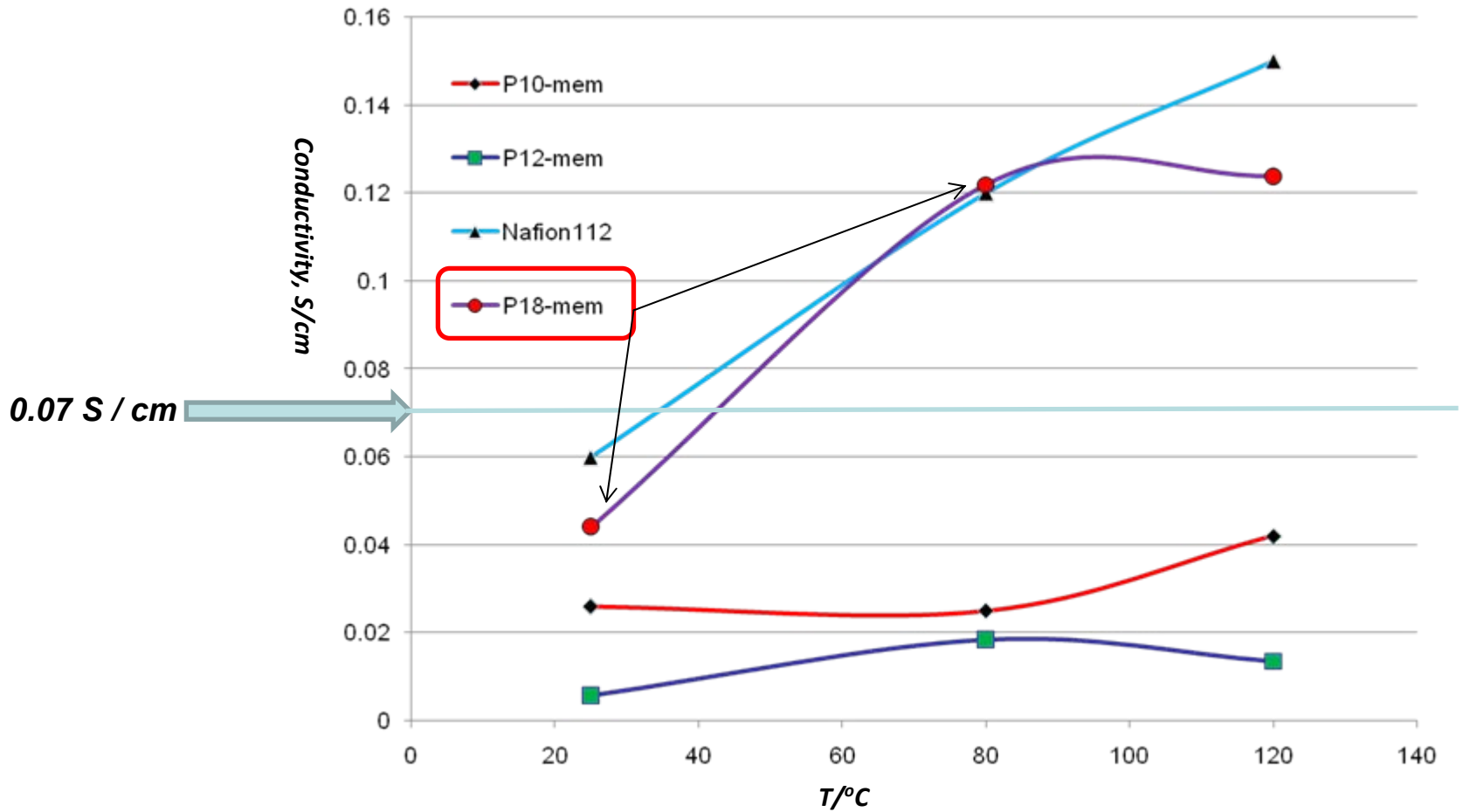
casting solutions



- Membrane from P18
- Flexible and tough
- Colorless
- Smooth and even

Copolymer from copolymerization  
of  $R_F\text{P}(\text{O})(\text{ONa})\text{CF}_3$  with TFE

**P18-mem**



*Proton conductivity data were acquired for ionomer samples at 100% RH at ambient, 80°C and 120°C. The membranes were hydrated by soaking in hot deionized water for 12h prior to study.*

# Summary of FPA ionomer studies

- Bis(fluoroalkyl)-phosphinic acid ionomers from monomer 11 ( $R_f = CF_3$ ) are readily prepared and have much improved properties over earlier generation ionomers from monomer 7 ( $R_f = C_4F_9$ ).
- Further improvements will be sought via low-EW ionomers from monomer 11, and via terpolymers with mixed FPA and FPA / sulfonimide monomers

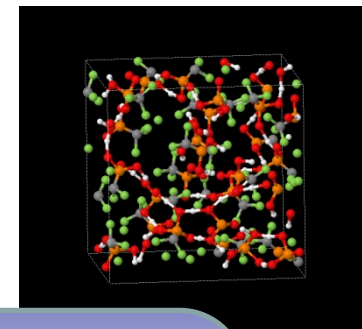
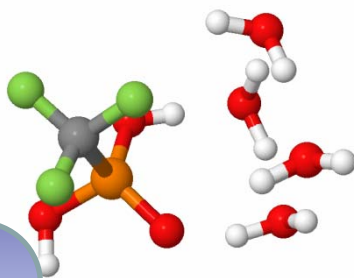
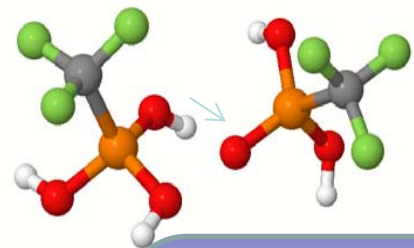
# Technical Accomplishments

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**FPA Electrolytes.**

**(2) Computer  
modeling**

# Simulations Approach

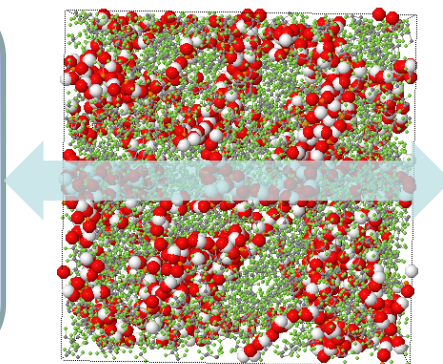


**Quantum Chemistry  
Calculations on  
Representative Gas-  
Phase Clusters**

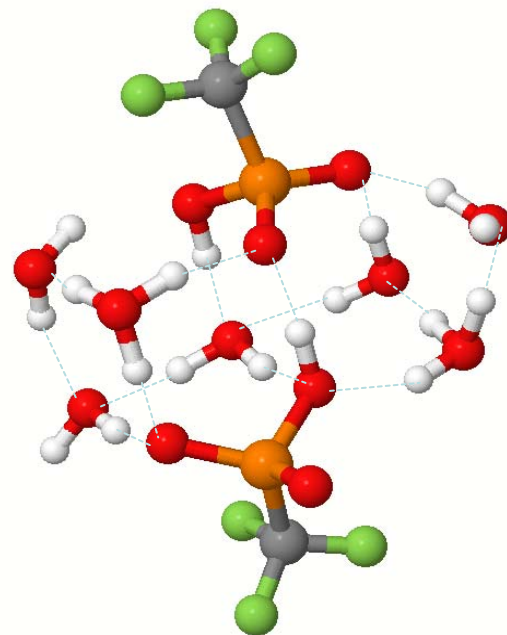
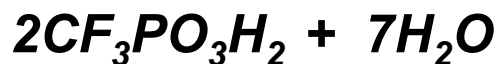
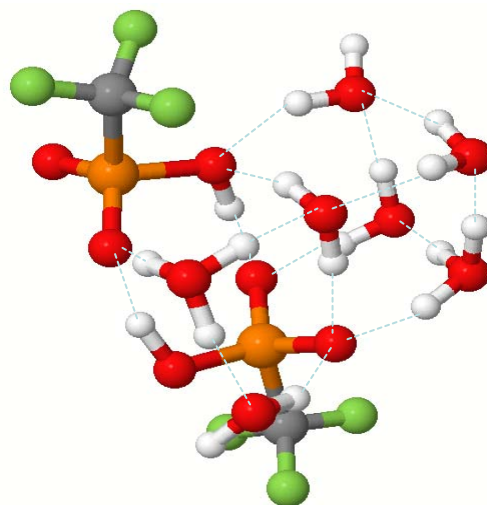
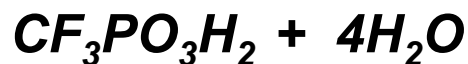
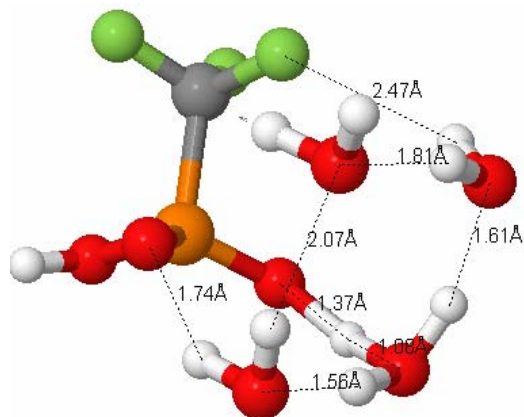
**DFT-based Born  
Oppenheimer Molecular  
Dynamics (BOMD)  
simulations using BLYP.  
27 molecules -  $\text{CF}_3\text{PO}_3\text{H}_2$   
24 molecules -  
 $(\text{CF}_3)_2\text{POOH}$**

**Classical MD  
simulations (no  
explicit proton  
hopping)  
(100s of molecules)**

**Classical MD  
simulations with  
explicit proton  
hopping (MS-EVB, Q-  
HOP)  
(100s of molecules)**



# Quantum Chemistry: How Many Waters are Needed to Deprotonate Acid Groups?

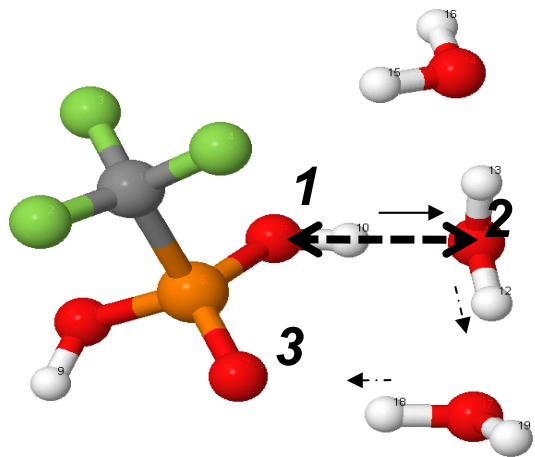


- *It takes 4 waters to deprotonate one phosphonic acid group, however, it takes only 7 waters to deprotonate 2 phosphonic acid groups*

*Calculations have been performed at mPW1PW91/6-31G(d,p)*



# Quantum Chemistry: Water-Mediated Internal Proton Transfer

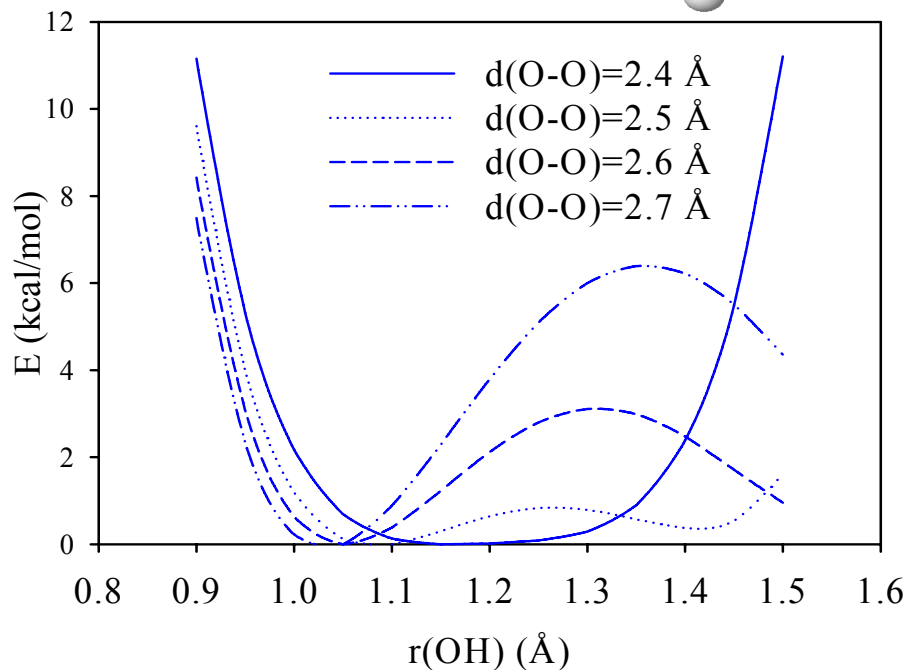


*The distance between an acid oxygen and water oxygen (donor-acceptor) is fixed to values (2.4 Å – 2.7 Å) and the barrier for the proton transfer between the donor and acceptor is studied using quantum chemistry calculations.*

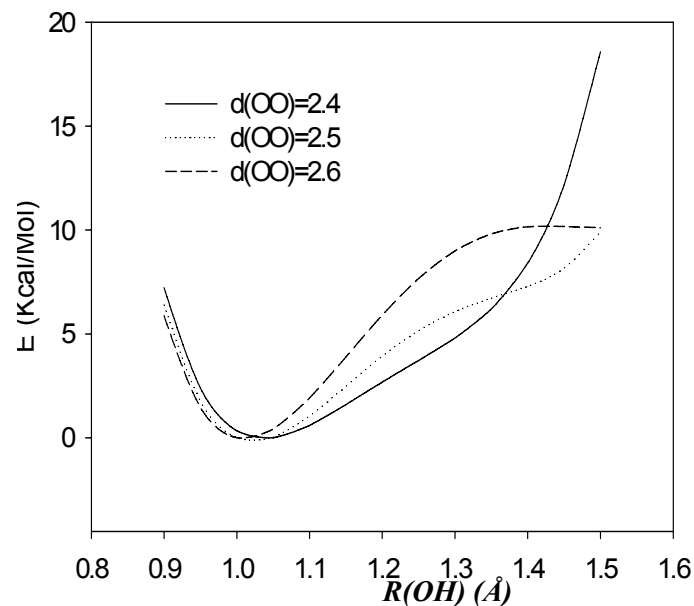
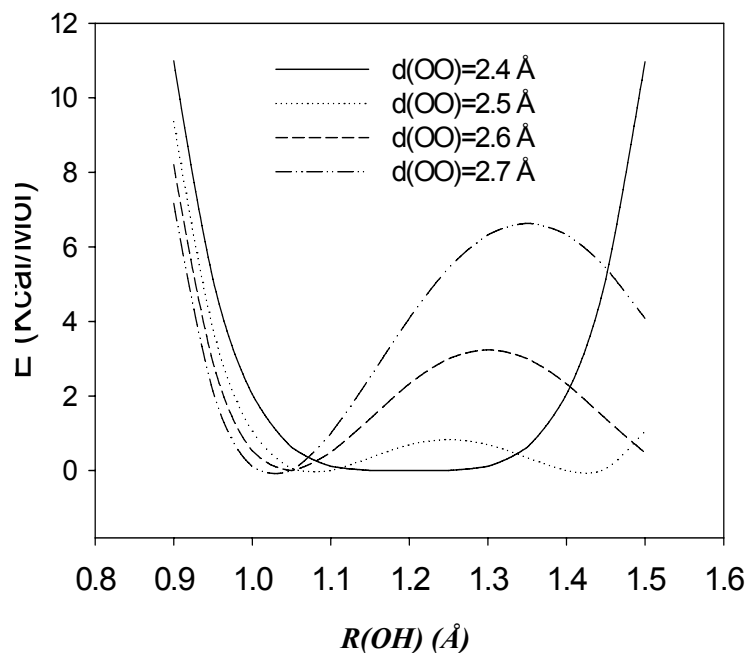
*Despite that in the FPA-(H<sub>2</sub>O)<sub>3</sub> cluster both acid protons are localized at the acid for the most energetically stable configuration. We find that there is a low barrier for the water mediated proton transport from one FPA oxygen to another.*

*As proton “1” shifts towards a water molecule, proton “2” shifts to the neighboring water, while proton “3” shifts towards the acid group resulting in an intermolecular water mediated proton transfer.*

*Results are shown for the mPW1PW91/6-31G\* level*



# Quantum Chemistry: Barriers for Proton Transfer

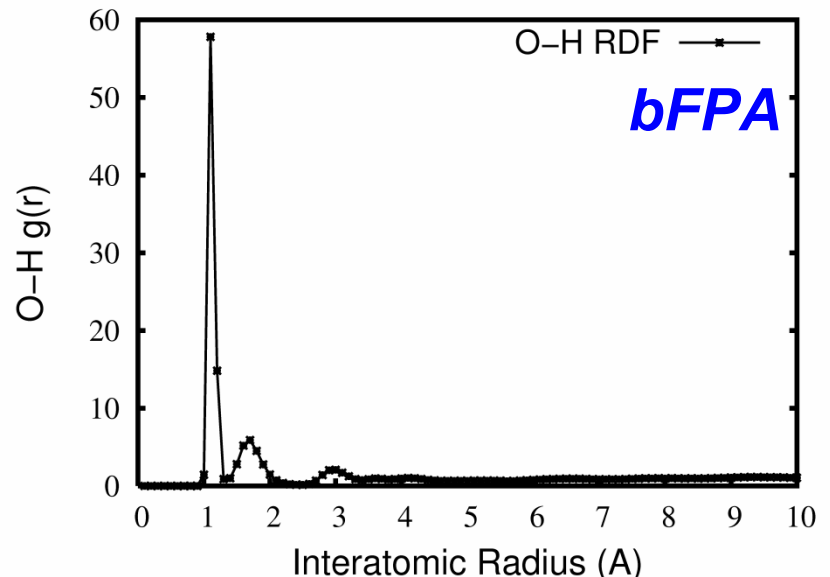
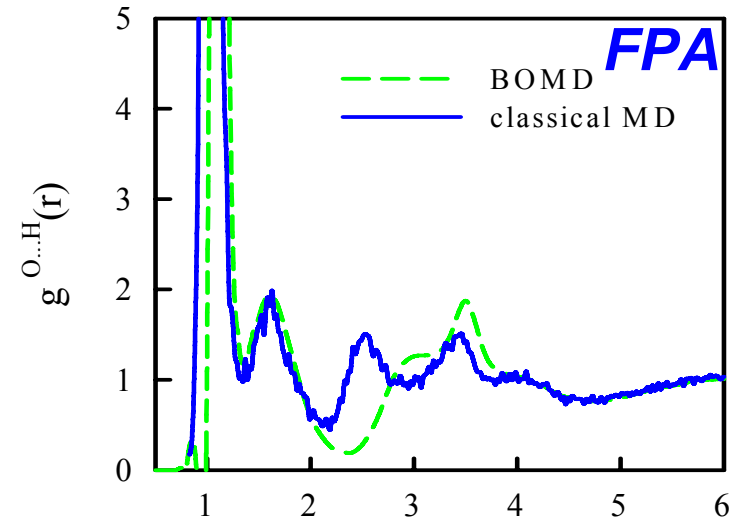


- **The barrier for proton transfer from  $CF_3PO_3H_3^+$  to  $CF_3PO_3H_2$  is much lower than from  $CF_3PO_3H_2$  to  $CF_3PO_3H^-$**
- **Barriers as a function of distance are used in MD simulations to incorporate explicit proton hopping**

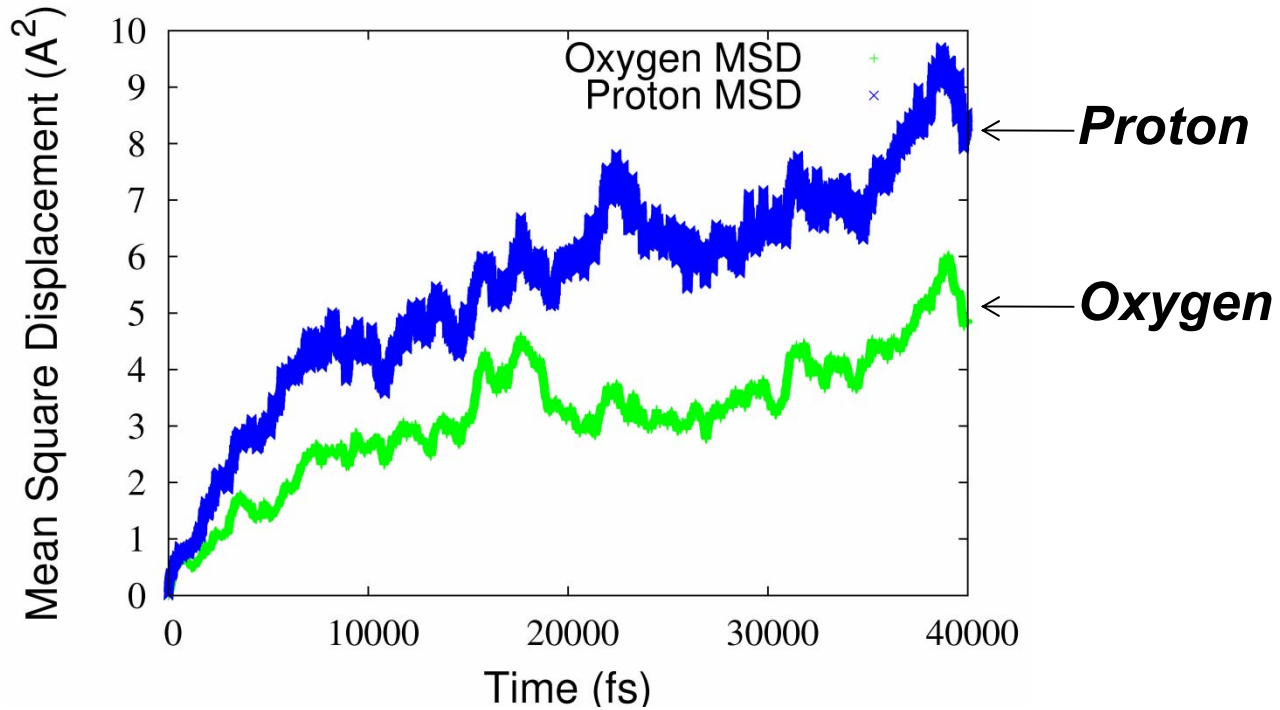
Calculations have been performed at mPW1PW91/6-31+G(d,p) level

# Born-Oppenheimer Molecular Dynamics:

- Trifluoromethyl phosphonic acid (FPA) ( $\text{CF}_3\text{PO}_3\text{H}_2$ ) system contains 27 molecules.
- *Bis*(trifluoromethyl) phosphinic acid (bFPA) ( $(\text{CF}_3)_2\text{POOH}$ ) system contains 24 molecules
- Equilibrated at 393K using classical force
- Born-Oppenheimer MD performed using BLYP DFT.
- 10ps of AIMD equilibration using temperature scaling.
- 40ps of NVE simulation time. (15ps complete for bFPA)
- AIMD and classical RDFs agree well, especially at short ranges.



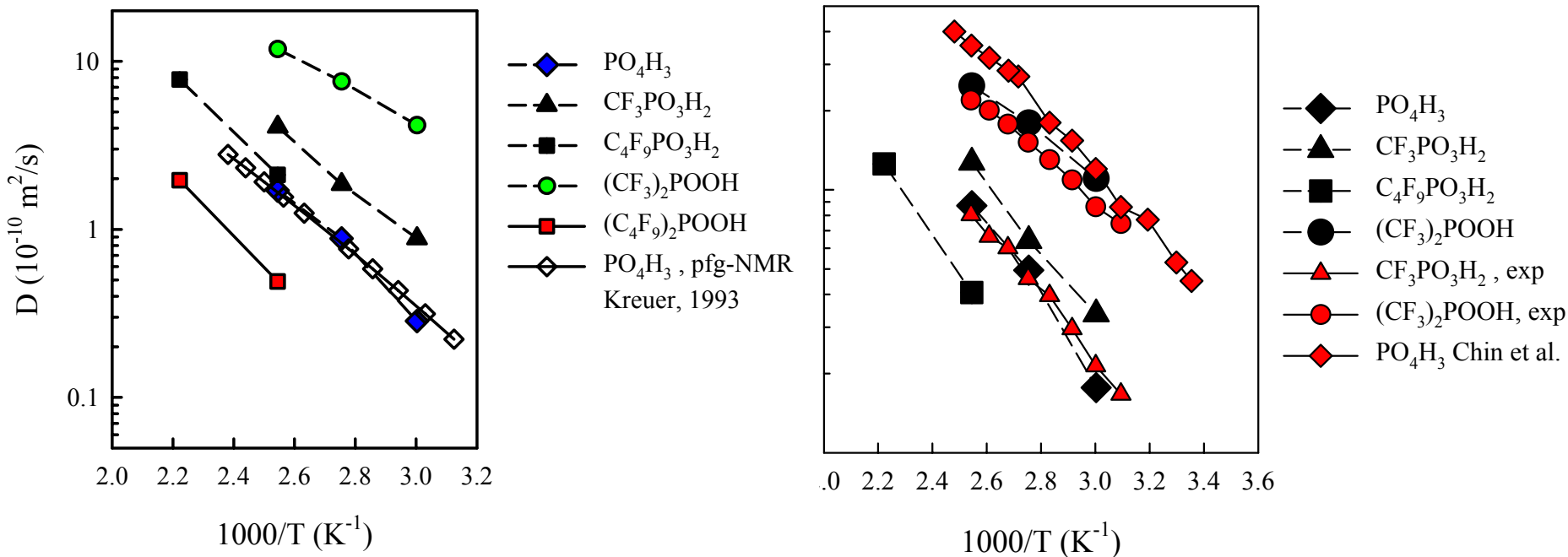
# Proton Transport in $CF_3PO_3H_2$



- **Proton diffusion is significantly faster than diffusion of the oxygen atoms to which the protons are nominally bonded.**
- **On average, autoionization exceeds **20%** at 393K.**
- **A significant Grotthuss component of PT is indicated.**

[Proton transport in  \$\(CF\_3\)\_2POOH\$  from BOMD simulations is currently under investigation](#)

# Conductivity Estimates from Classical MD

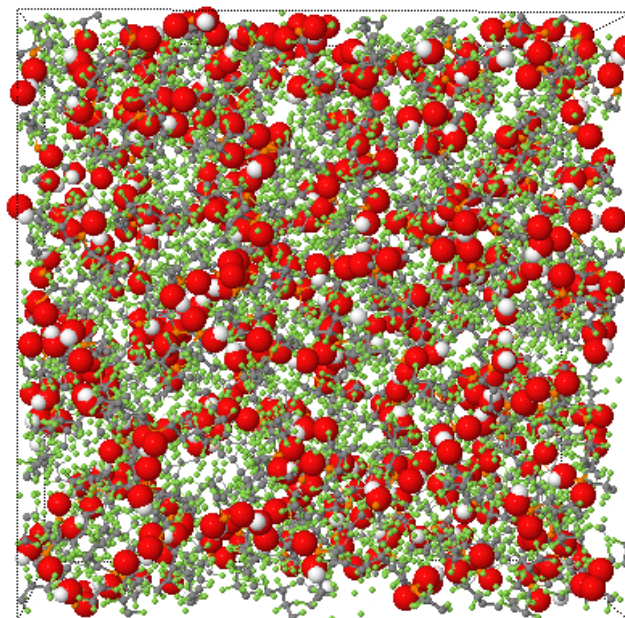
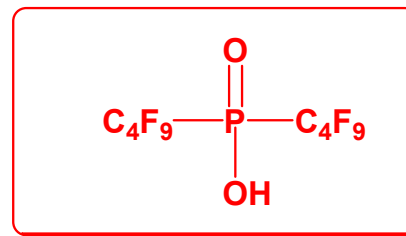
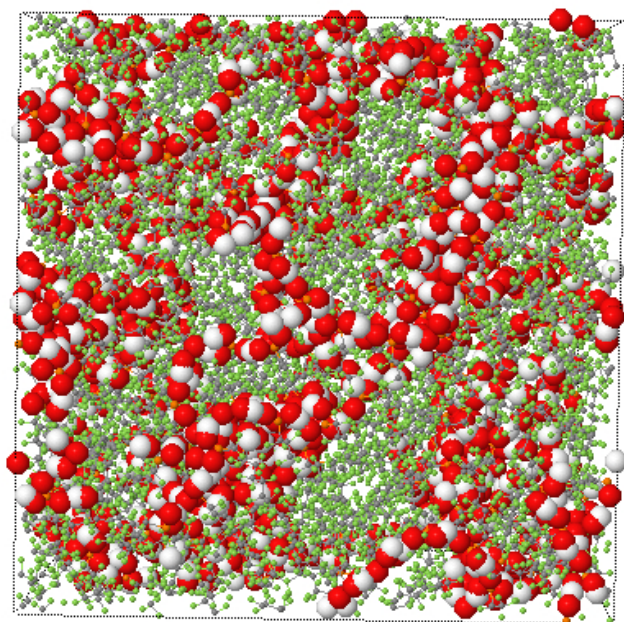
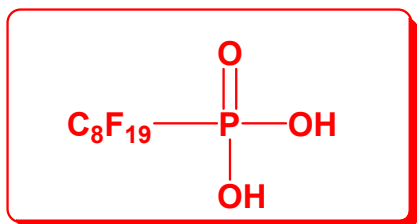


**If conductivity is estimated from classical MD simulations assuming complete acid self-dissociation and no ion correlations and no Grotthuss mechanism for proton transfer, one observes:**

**•orthophosphoric acid: experimental value is much larger than estimate from classical MD indicating that the Grotthuss mechanism is dominating proton transfer;**

**•fluorophosphonic acid and bis-fluorophosphonic acids: experimental data are closer to MD estimates indicating that Grotthuss proton transfer is less efficient in these acids than in  $\text{PO}_4\text{H}_3$**

# Aggregation of acid groups



Jmol

*Hydrogen and oxygen have been increased in size to highlight acid group aggregation*

*$C_8F_{17}PO_3H_2$  exhibits good acid group aggregation giving rise to possible proton conducting pathways, while  $(C_4F_9)_2POOH$  does not exhibit acid group aggregation*

# Future work

- Conductivity studies on small-molecule FPA model compounds will focus on low water contents and on mixtures of FPAs with superacids (e.g. sulfonamide acids) as models for terpolymer ionomers
- PFG NMR studies on FPAs will measure atom self-diffusion coefficients to evaluate Grotthuss conduction.
- Water uptake studies on FPAs will be pursued at variable RH
- Ionomer studies will focus on lower EW ionomers, terpolymers, and on strategies for stabilizing H-bonded proton transport pathways.
- MD simulations (MS-EVB or Q-hop) will focus on acid-water mixtures with explicit proton hopping included