



Highly Stable Anion-Exchange Membranes for High-Voltage Redox-Flow Batteries



2016 DOE Hydrogen and Fuel Cells Program Review

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FC131

June 8, 2016

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start: June 1, 2015
- End: May 31, 2017
- % complete: ~45%

Budget (\$K)

- UD, \$500 K
- NREL, \$100 K
- Total Project Budget \$750K
(\$600K DOE Share + \$150K Cost Share)

Barriers

- Durability (Oxidative Stability of Membrane)
- Performance (Ion Conductivity)
- Cost

Partners – Principle Investigators

- University of Delaware – Yushan Yan, Shuang Gu, Bingjun Xu
- National Renewable Energy Laboratory – Bryan Pivovar

Relevance

Objectives & Relevance

Objectives:

- Develop a class of anion-exchange membranes (AEMs) with very high oxidation resistance for high-voltage cerium redox-flow batteries (RFBs), and other alkaline membrane-based electrochemical devices such as fuel cells and electrolyzers
- Gain new knowledge of polymer chemistry and membrane technology that will help advance the design and development of polymer electrolytes for electrochemical devices

Relevance:

- With voltages more than double the voltage of standard all-vanadium RFBs, cerium RFBs hold the potential to offer high-performance and low-cost electricity storage solution for renewable energy.
- Stable AEMs can also be used for hydroxide exchange membrane fuel cells (HEMFCs), which will improve the cell durability and performance (e.g., operating at elevated temperatures). Another potential application of stable AEMs is in alkaline membrane electrolyzers for renewable hydrogen production.
- Stable AEMs are the key missing element in making cerium RFBs a viable technology. Stable membranes are also necessary to achieve highly durable AEM electrolyzers, which will lower the cost for hydrogen production.

Approach

Project Milestones

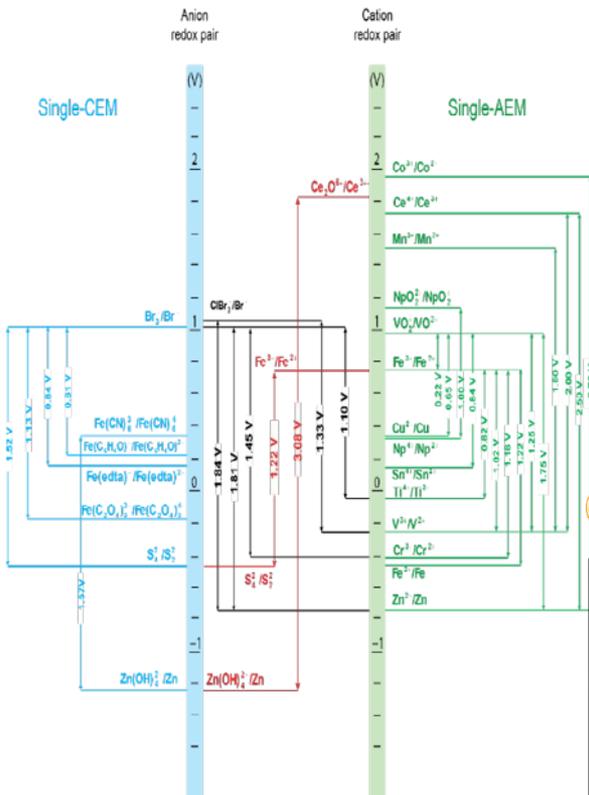
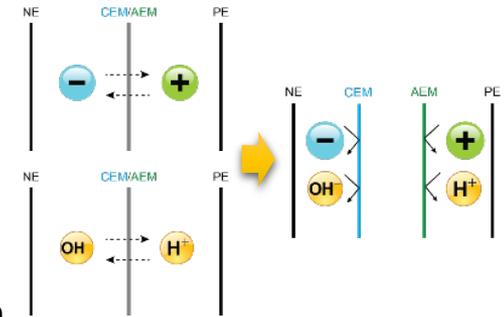
| No. | Due Date | Milestones | Status |
|------|------------|--|-------------------|
| M1.1 | 10/30/2015 | Less than 10% loss of initial weight for the identified polymer at 40 °C for 1000 h in 0.5 M Ce(IV)(ClO ₄) ₄ | Completed on time |
| M1.2 | 1/31/2016 | Less than 5% of multiple brominated 9MeTTP ⁺ cation based on ¹ H and ³¹ P NMR spectroscopy | Completed on time |
| M1.3 | 4/30/2016 | More than 95% purity for synthesized 9MeTTP ⁺ - functionalized polymers based on ¹ H and ³¹ P NMR spectroscopy | Completed on time |
| M1.4 | 7/31/2016 | Less than 20% loss of initial IEC for 9MeTTP ⁺ - functionalized polymers at an accelerated degradation test at 40 °C for 1000 h in 0.5 M Ce(IV)(ClO ₄) ₄ | To be performed |

Approach

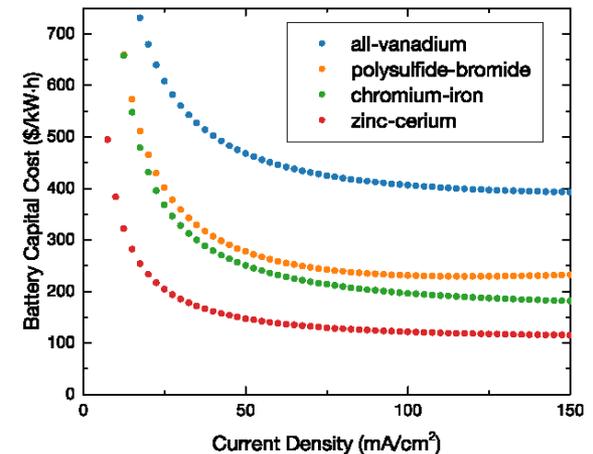
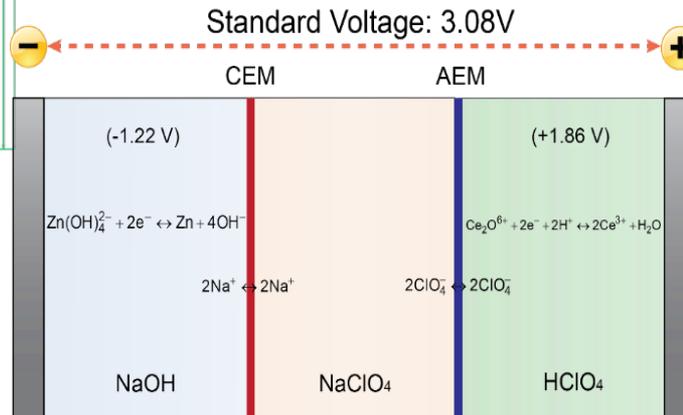
High voltage aqueous redox flow batteries, ARPA-E OPEN 2012

Concept of double-membrane RFB

- Single-membrane design
 - Cannot effectively separate anion and cation
 - Cannot effectively separate acid and base
- Requires double-membrane design

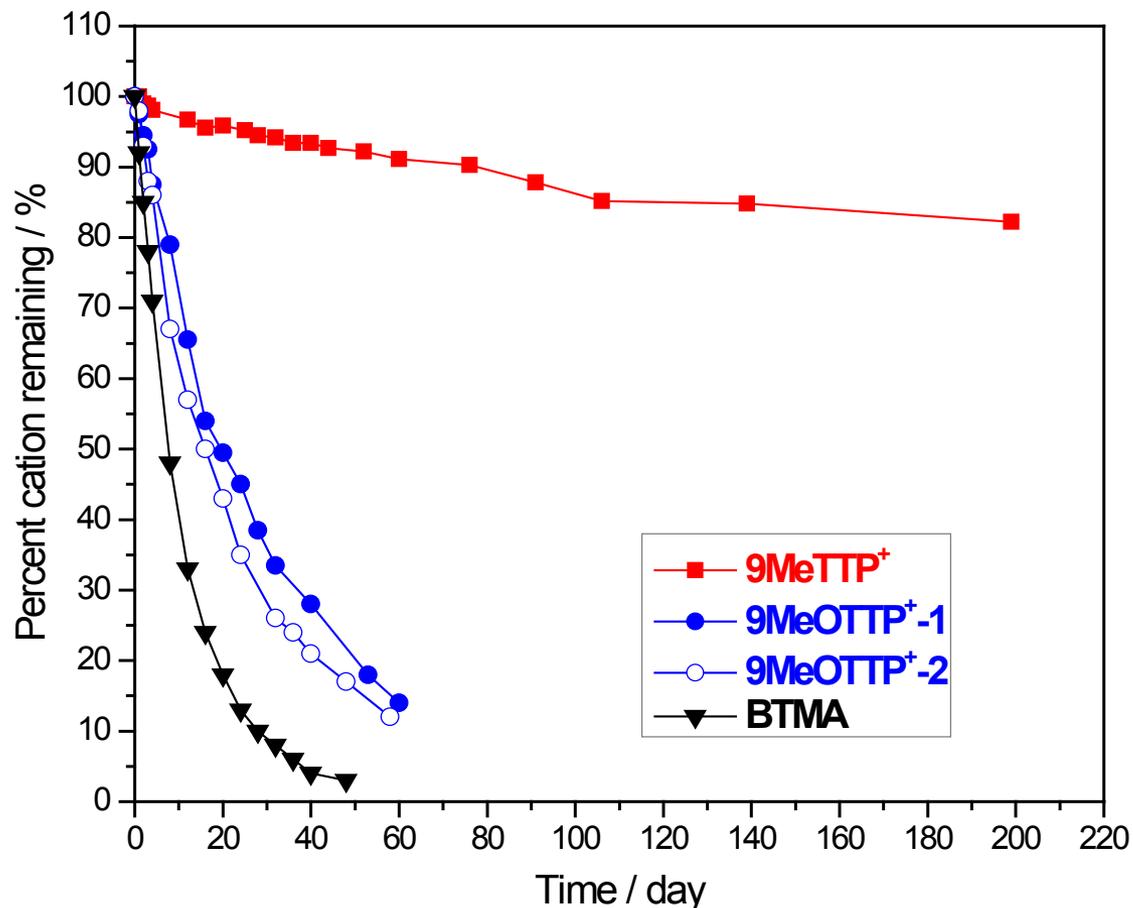


Zn-Ce RFB

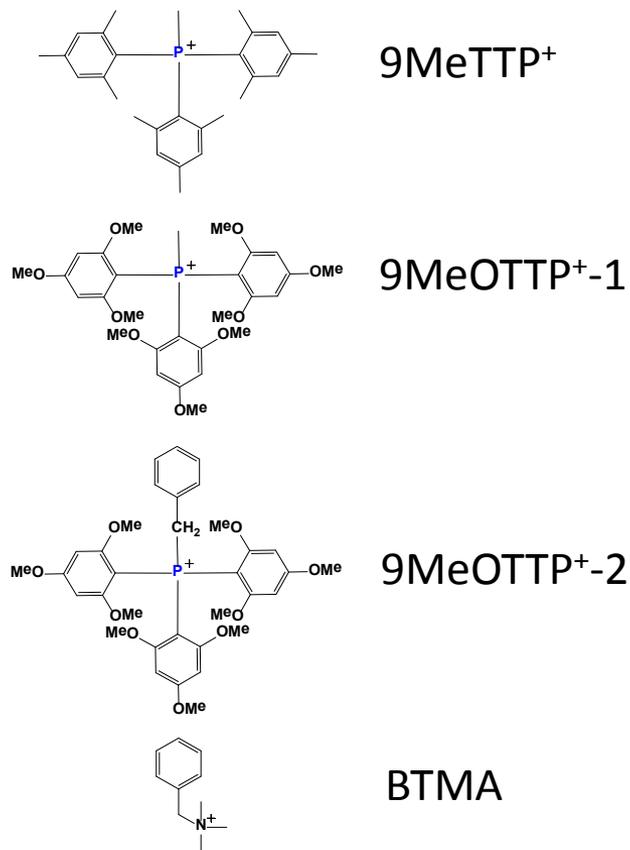


Approach

Alkaline Stability of 9MeTTP⁺



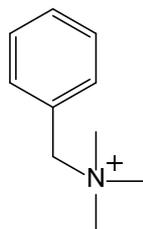
1 M KOD solution, 80 °C, MeOD/D₂O = 5/1 (vol). ³¹P NMR spectroscopy was used to determine the degree of degradation for all phosphonium cations, and ¹H NMR spectroscopy for ammonium cation.



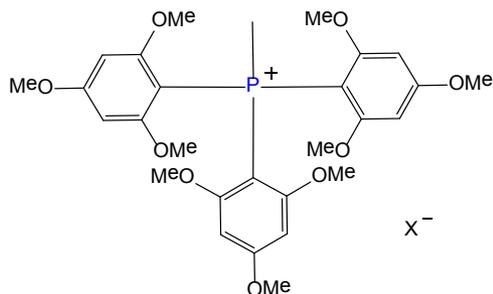
Approach

Oxidation Stability of 9MeTTP⁺

BTMA



9MeOTTP⁺

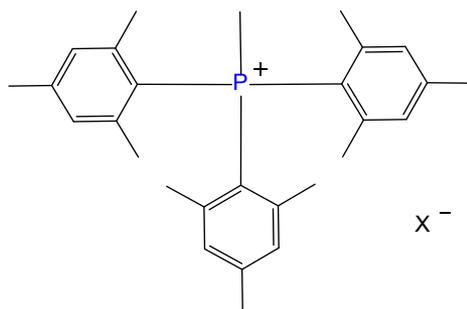


X⁻



Highly
oxidation-
resistant
Phosponium
cation

9MeTTP⁺



X⁻

A



B



C



Test conditions: 10 mM as test cation concentration, 0.3 M Ce(IV)(ClO₄)₄ containing 0.1 M HClO₄ as test cerium electrolyte, **20 °C as test temperature**, and 12 h as test time.

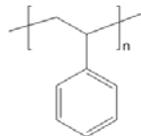
(A) **BTMA⁺**-containing solution sample before the stability test (left) and after the test (right).

(B) **9MeOTTP⁺**-containing solution sample before the stability test (left) and after the test (right).

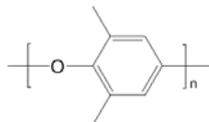
(C) **9MeTTP⁺**-containing solution sample before the stability test (left) and after the test (right).

Accomplishments and Progress

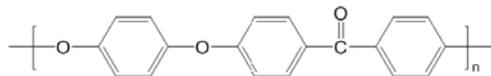
Polymer Backbone Oxidation Stability test result



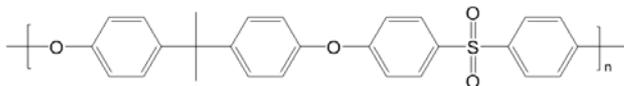
Polystyrene (PS)



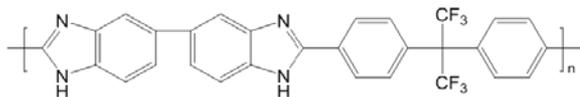
Poly(2,6-dimethyl-phenylene oxide) (PPO)



Poly(ether ether ketone) (PEEK)



Polysulfone (PSf)



Hexafluoroisopropylidene polybenzimidazole (6FPBI)

| | Weight loss (%) at 500 h | Weight loss (%) at 1000 h | Morphography change |
|-------|--------------------------|---------------------------|---------------------|
| PS | 0 | 5 | No |
| PPO | 10 | 30 | Cloudy and Brittle |
| PSf | 0 | 0 | No |
| PEEK | 0 | 0 | No |
| 6FPBI | 0 | 0 | No |

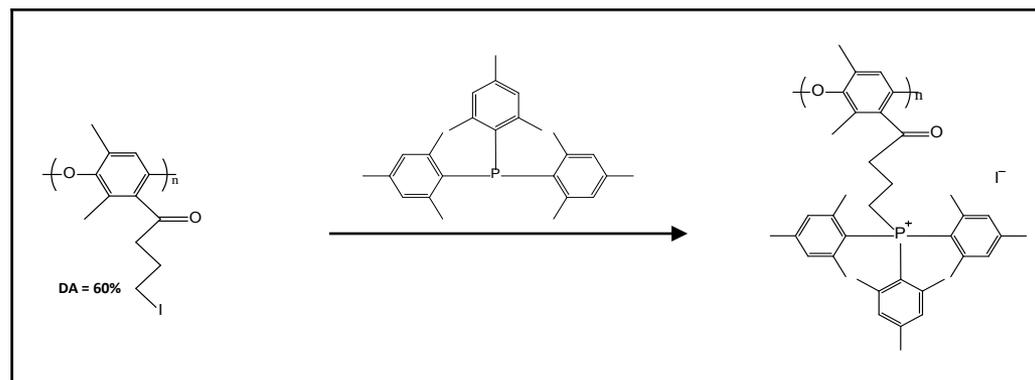
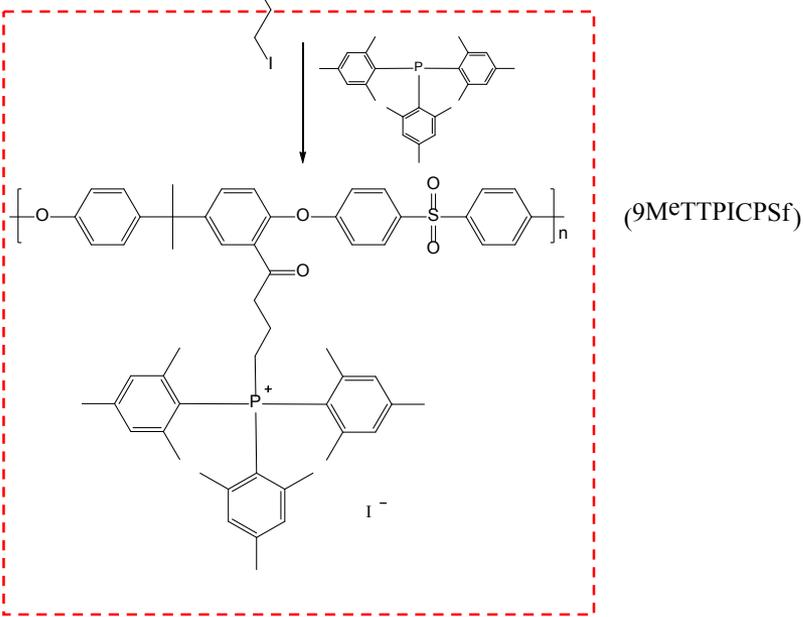
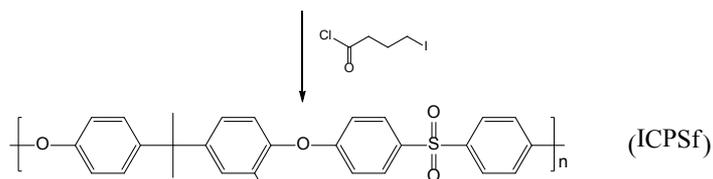
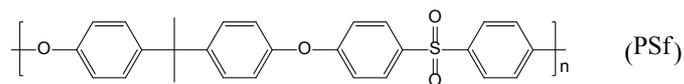
Stability test of polymer membranes:

the weight of dry PSf membrane (W_1 , g) was measured first, and then the membrane was immersed in 0.5 M $Ce(IV)(ClO_4)_4$ solution at 40 °C. After 500 h and 1000 h, the membrane was taken out and washed with DI water several times to remove the residual salts. The weight of the membrane (W_2 , g) was measured after drying under vacuum at 80 °C for 24 h. The weight loss (WL) of membrane was calculated by:

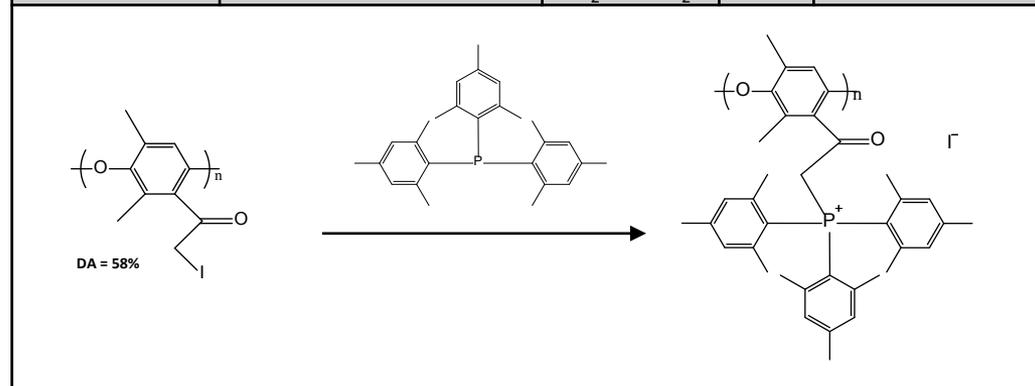
$$WL (\%) = (W_1 - W_2) / W_1 \times 100\%$$

Accomplishments and Progress

Proposed Direct Quaternization through Central Phosphorus Atom



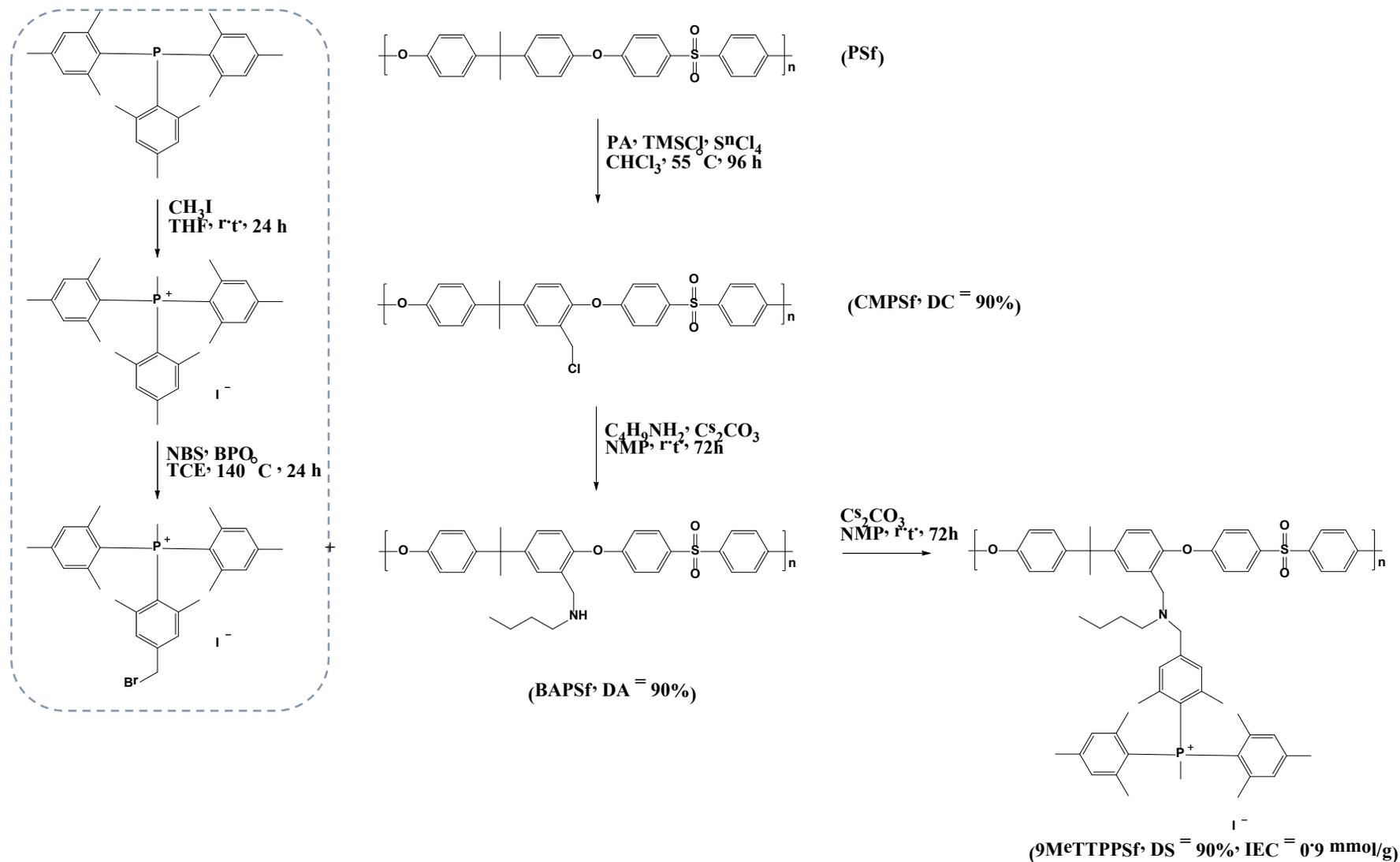
| Temperature | Molar ratio (phosphine/polymer) | Solvent | Time | Degree of quaternization |
|-------------|---------------------------------|--------------------------------------|------|--------------------------|
| 60 °C | 2 | CHCl ₃ | 5 h | 0 |
| 80 °C | 2 | ClCH ₂ CH ₂ Cl | 5 h | 0 |
| 80 °C | 5 | ClCH ₂ CH ₂ Cl | 24 h | 0 |
| 120 °C | 2 | Cl ₂ CHCHCl ₂ | 5 h | 0 |



| Temperature | Molar ratio (phosphine/polymer) | Solvent | Time | Degree of quaternization |
|-------------|---------------------------------|--------------------------------------|------|--------------------------|
| 20 °C | 2.5 | CHCl ₃ | 12 h | 0 |
| 60 °C | 2.5 | CHCl ₃ | 12 h | 0 |
| 80 °C | 2.5 | ClCH ₂ CH ₂ Cl | 12 h | 0 |

Accomplishments and Progress

New Proposed Synthetic Strategy for Attaching 9MeTTP⁺ Cation to PSf



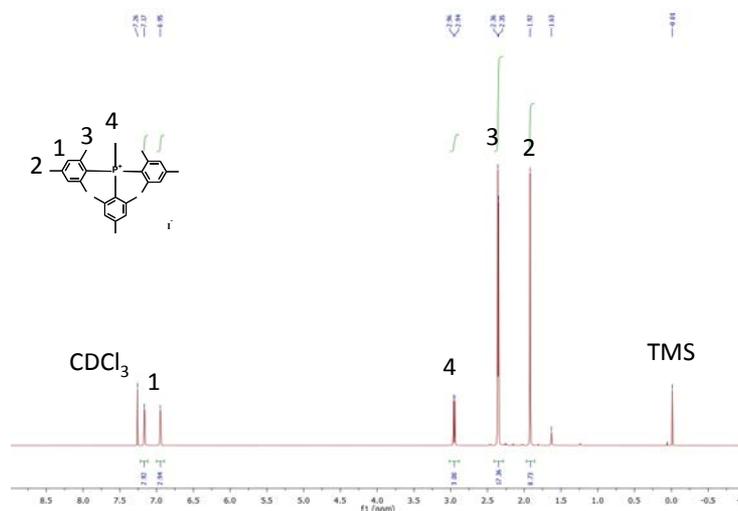
Accomplishments and Progress

Bromination of 9MeTTP⁺ cation investigation

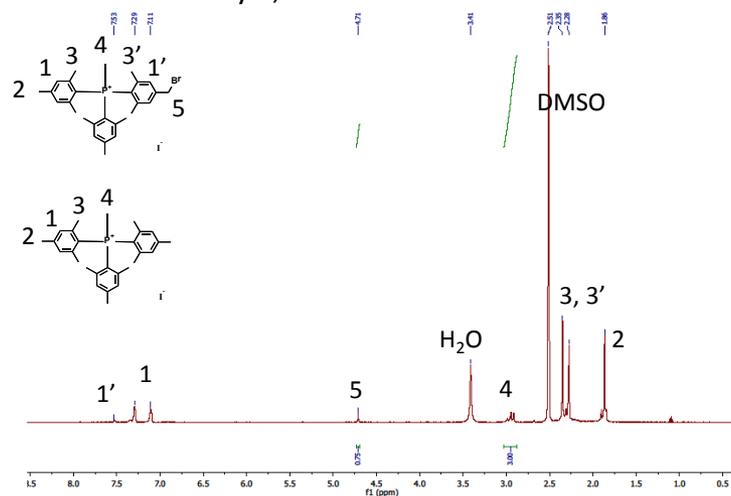
| Entry | 9MeTTP ⁺ (mmol) | NBS ^a (mmol) | BPO ^b (mmol) | TCE ^c (ml) | T (°C) | Time (hour) | DB ^d (%) |
|-------|-------------------------------|----------------------------|----------------------------|--------------------------|-----------|----------------|------------------------|
| 1 | 1 | 1 | 0.05 | 10 | 80 | 24 | 0 |
| 2 | 1 | 1 | 0.05 | 10 | 140 | 24 | 5 |
| 3 | 1 | 1 | 0.05 | 10 | 140 | 48 | 5 |
| 4 | 1 | 1 | 0.1 | 20 | 100 | 20 | 0 |
| 5 | 1 | 1.5 | 0.15 | 20 | 100 | 20 | 0 |
| 6 | 1 | 1.5 | 0.15 | 20 | 80 | 20 | 0 |
| 7 | 1 | 2 | 0.2 | 12 | 140 | 24 | 25 |
| 8 | 1 | 3 | 0.3 | 10 | 140 | 24 | 30 |
| 9 | 1 | 3 | 0.3 | 3 | 140 | 24 | 33 |
| 10 | 1 | 5 | 0.5 | 12 | 140 | 24 | 40 |
| 11 | 1 | 5 | 0.5 | 10 | 140 | 24 | 50 |
| 12 | 1 | 5 | 0.5 | 3 | 140 | 24 | 100 |

- a.** N-Bromosuccinimide (NBS) was used as bromination reagent;
b. Benzoyl peroxide (BPO) was used as radical initiator;
c. Tetrachloroethane (TCE) was used as solvent;
d. Degree of total bromination.

¹H NMR, CDCl₃ solvent

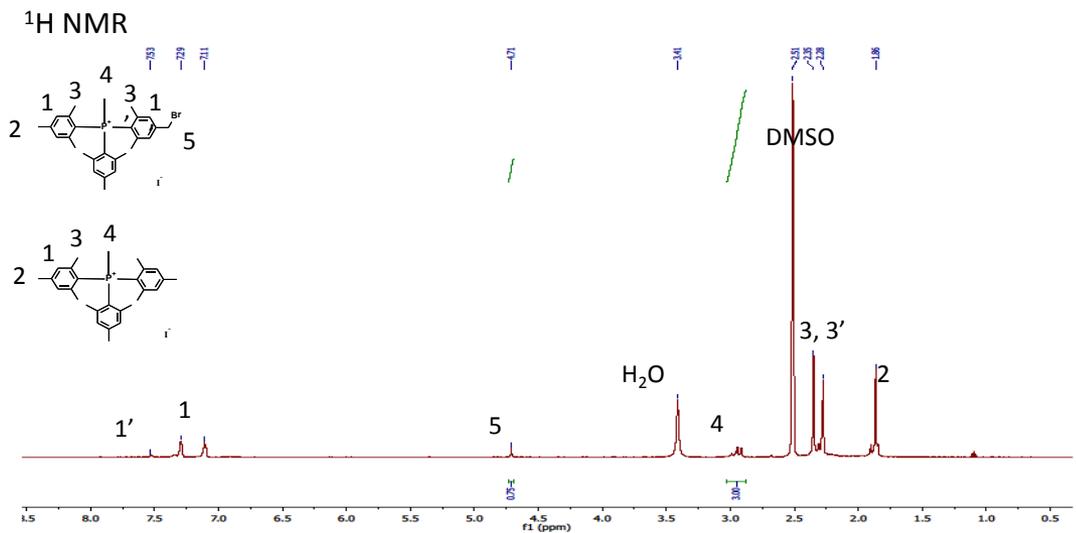


¹H NMR of Entry 9, DMSO solvent



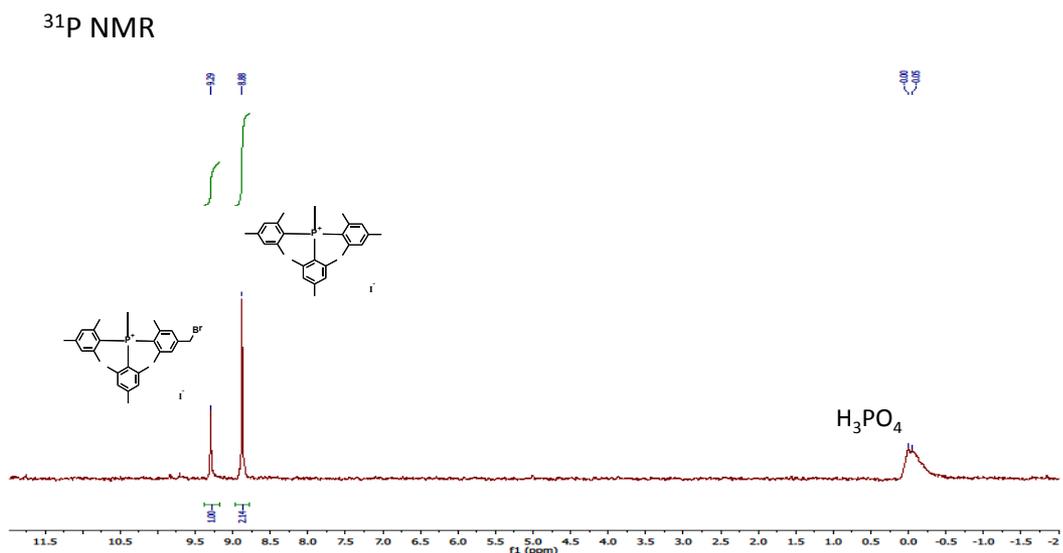
Accomplishments and Progress

Bromination of 9MeTTP⁺ cation result



- In ¹H NMR spectrum, the peak at 4.71 ppm indicate the methylene group adjacent to bromine and benzene. The degree of bromination (DB) is calculated from the ¹H NMR spectrum as the following equation:

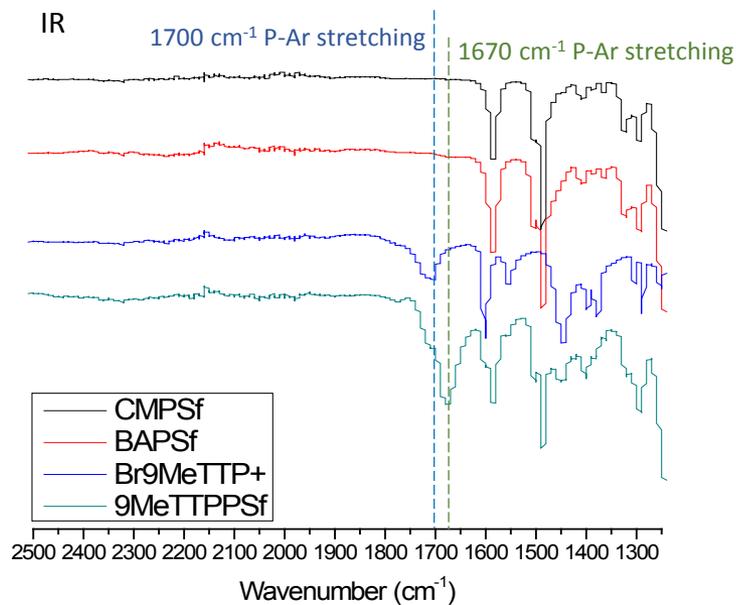
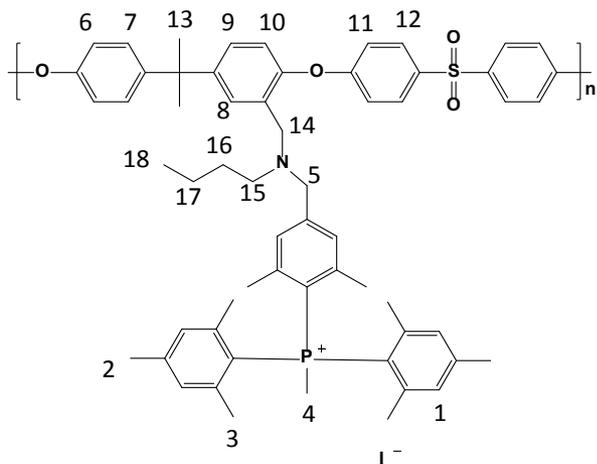
$$DB = \frac{3A_5}{2A_4} \times 100\%$$



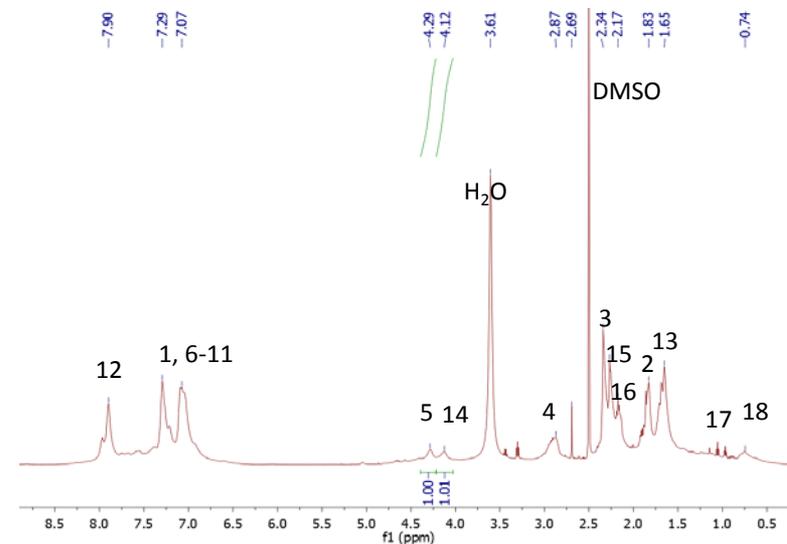
- In ³¹P NMR spectrum, there are two peaks indicate mono-brominated 9MeTPP⁺ cation and non-brominated 9MeTPP⁺ cation respectively. The integration ratio of these 2 peaks is approximately 1:2, which is consistent with the 33% DB. No signal of the multiple brominated 9MeTPP⁺ cation can be found.

Accomplishments and Progress

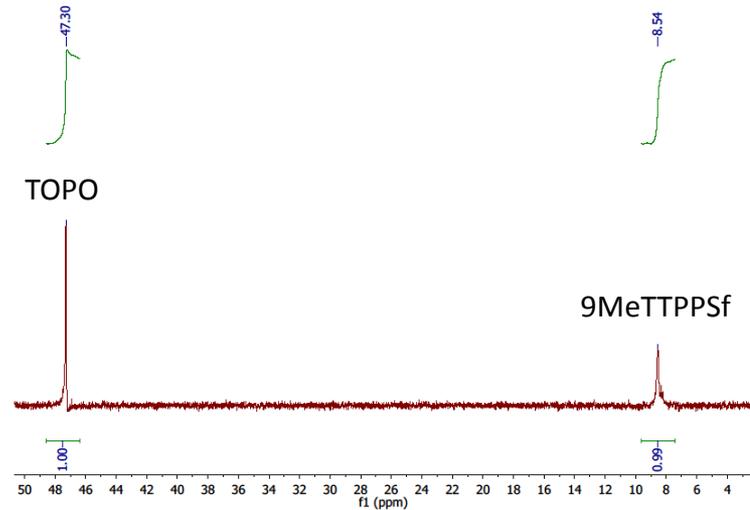
9MeTTP⁺ - functionalized polymer



¹H NMR

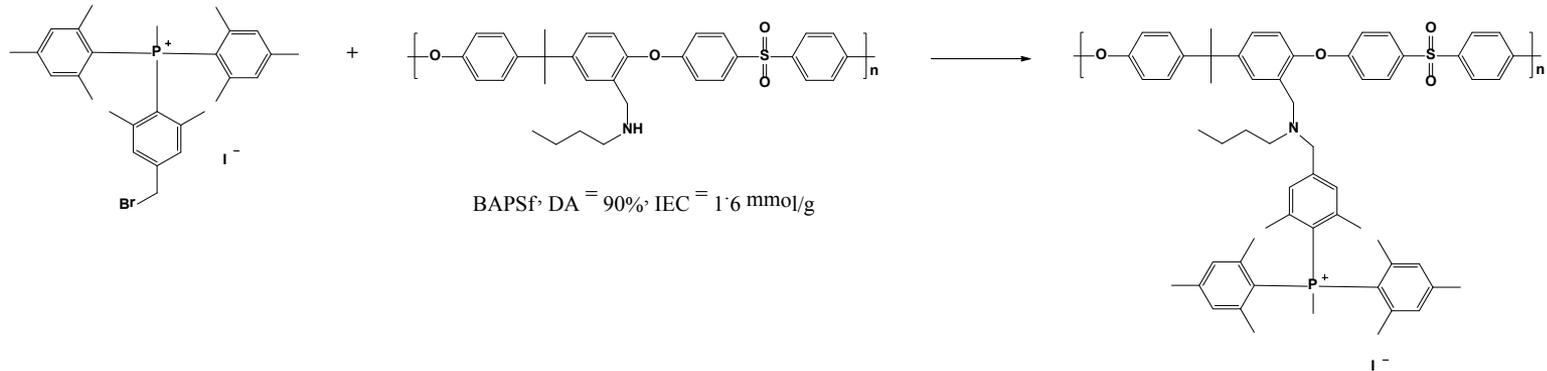


³¹P NMR



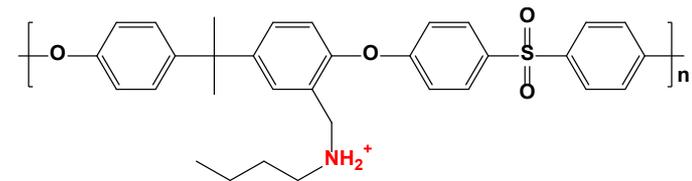
Accomplishments and Progress

BAPSF membrane oxidation stability test



| | Weight loss (%) at 500 h | Weight loss (%) at 1000 h | Morphography change |
|-------|--------------------------|---------------------------|---------------------|
| PS | 0 | 5 | No |
| PPO | 10 | 30 | Cloudy and Brittle |
| PSf | 0 | 0 | No |
| PEEK | 0 | 0 | No |
| 6FPBI | 0 | 0 | No |

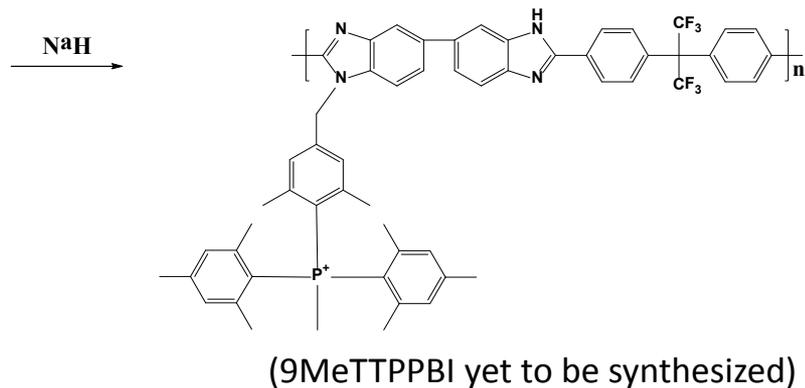
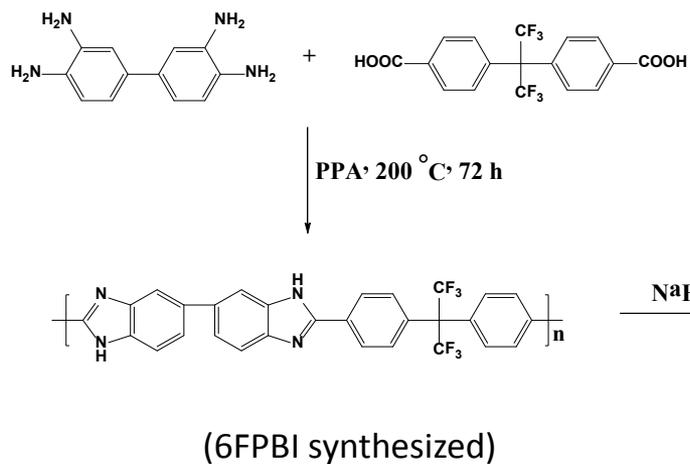
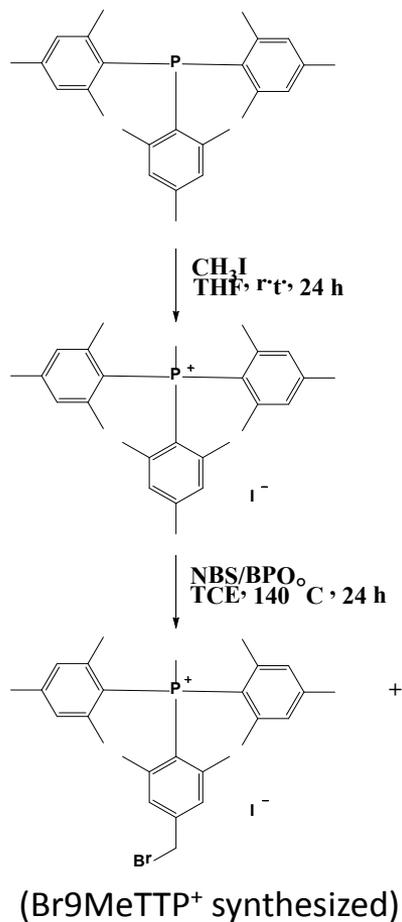
| | 200 h | 400 h |
|-------------------|---------------------------|-------|
| BAPSF (IEC = 1.6) | ~10% degradation in H NMR | break |



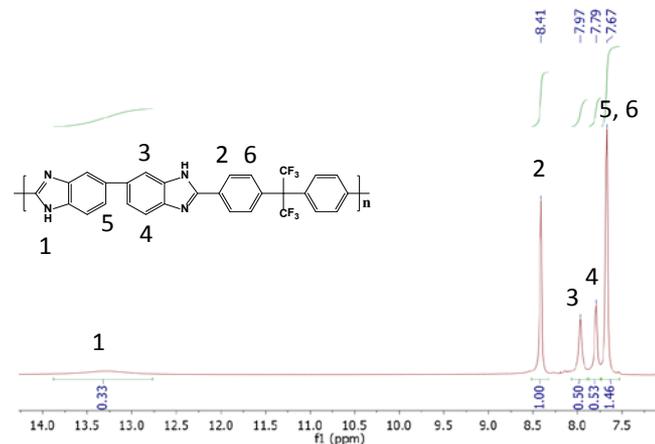
BAPSF ($\text{IEC} = 1.6 \text{ mmol/g}$) in 0.3 M
 $\text{Ce}(\text{ClO}_4)_4$ and 0.1 M HClO_4

Accomplishments and Progress

9MeTTP⁺ - functionalized polymer based on 6FPBI backbone



¹H NMR 6FPBI



Collaborations

| Institutions | Role |
|---|--|
| <u>University of Delaware:</u> Yushan Yan (PI), Shuang Gu, Bingjun Xu | Prime; Oversees the project, lead AEM synthesis and characterization |
| <u>National Renewable Energy Laboratory (NREL):</u> Bryan Pivovar (PI) | Sub; Test membrane durability and prepare MEA and MEA testing |

Future Work/Remaining Challenges

9MeTTP⁺ Bromination:

- Increase the degree of single bromination
- Avoid multiple bromination product in large scale synthesis

Polymer Backbone:

- Overcome compromised oxidation stability due to hydrophilic functional groups

Membrane Casting:

- Address the brittle membrane due to crosslinking and large sized 9MeTTP⁺ cation

RFB/Fuel Cell Testing:

- Test 9MeTTP⁺ - functionalized polymer membranes in RFB/Fuel Cell

Summary

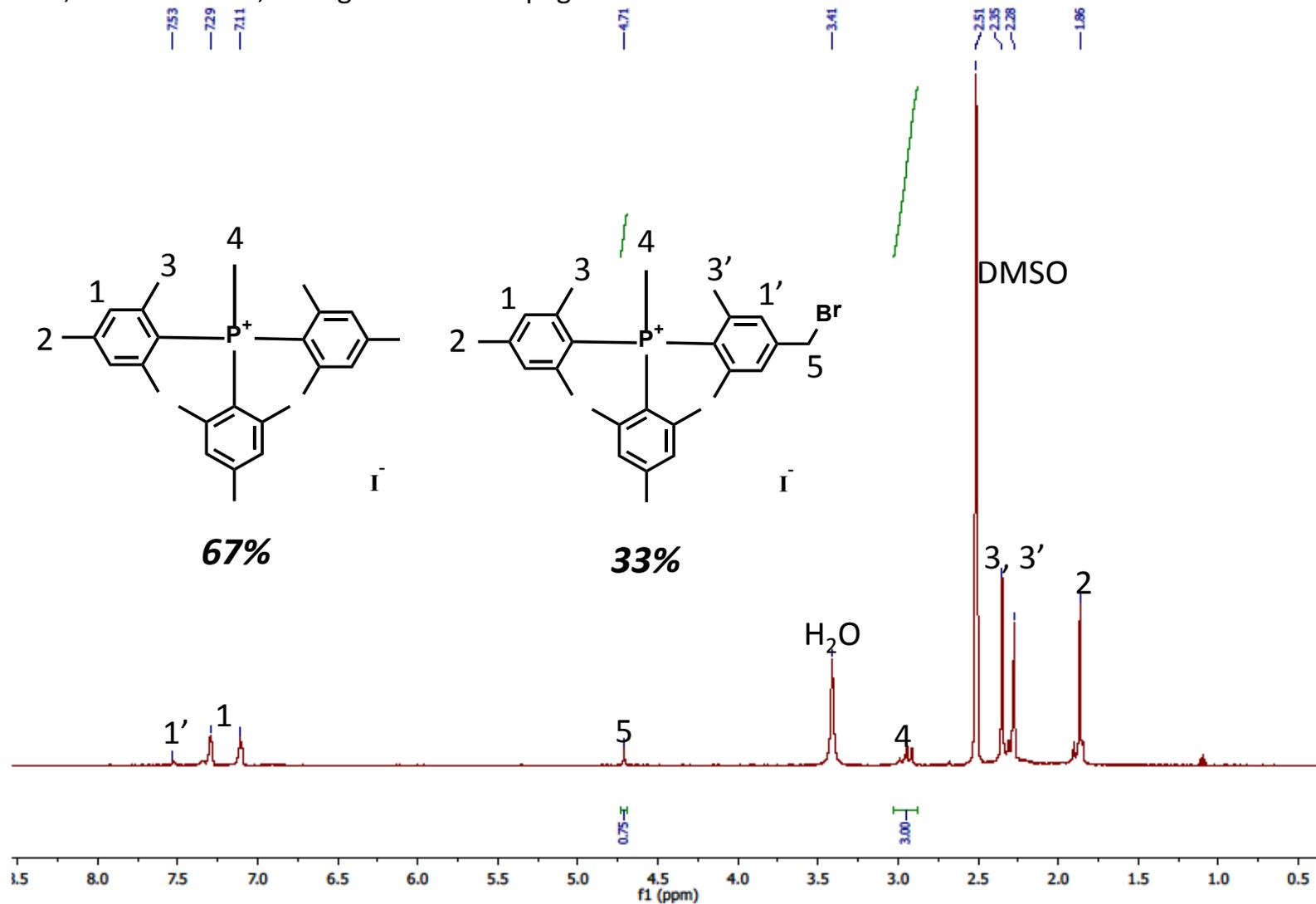
- Relevance: Developing highly stable anion-exchange membranes for high-voltage redox-flow batteries.
- Approach: Developing anion-exchange membrane based on 9MeTTP⁺ cation.
- Accomplishments and Progress: The project has explored multiple chemistries for connecting 9MeTTP⁺ to a commercial polymer backbone. The direct quaternization method through central phosphorus atom has been proved to be infeasible due to the high steric hindrance of the 9MeTTP molecule. We have devised a new synthesis strategy through brominated 9MeTTP⁺ cation, and obtained the desired 9MeTTP⁺ - functionalized polysulfone. In order to further improve the oxidation stability of the polymer, a 9MeTTP⁺ - functionalized 6FPBI polymer is under investigation.
- Collaborations: We have obtained some new polymers from RPI that might be stable toward oxidation.
- Future Research: Focus on improving the conversion of the bromination of 9MeTTP⁺; improve the membrane property; and explore other MeTTP⁺ that may be more conducive to mono-bromination with high conversion.

Technical Backup Slides

Accomplishments and Progress

Bromination of 9MeTTP⁺ cation

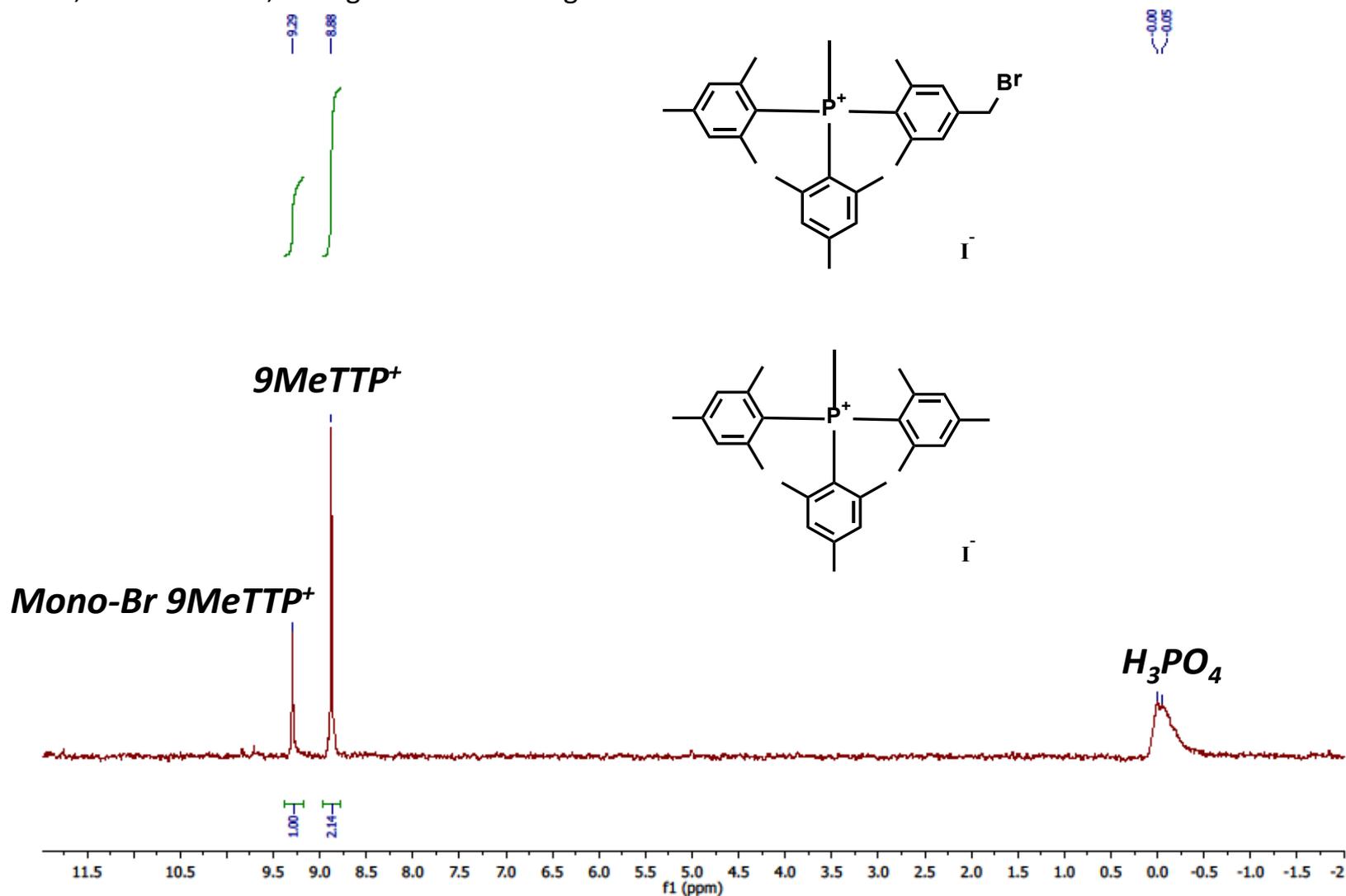
¹H NMR, DMSO solvent, enlarged of NMR in page 11



Accomplishments and Progress

Bromination of 9MeTTP⁺ cation

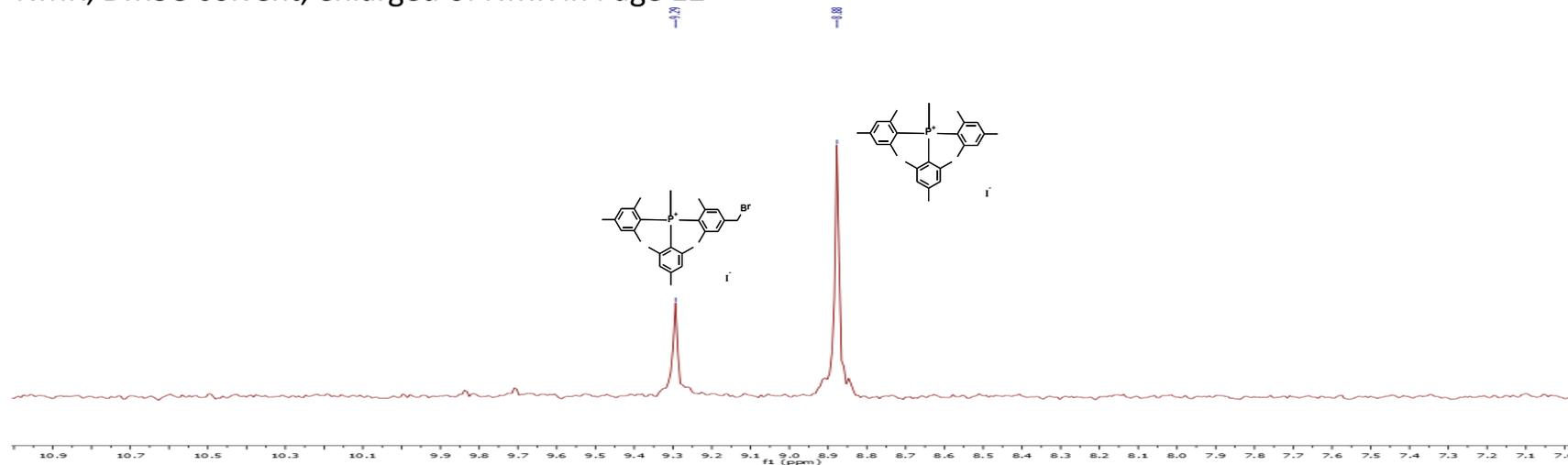
³¹P NMR, DMSO solvent, enlarged of NMR in Page 12



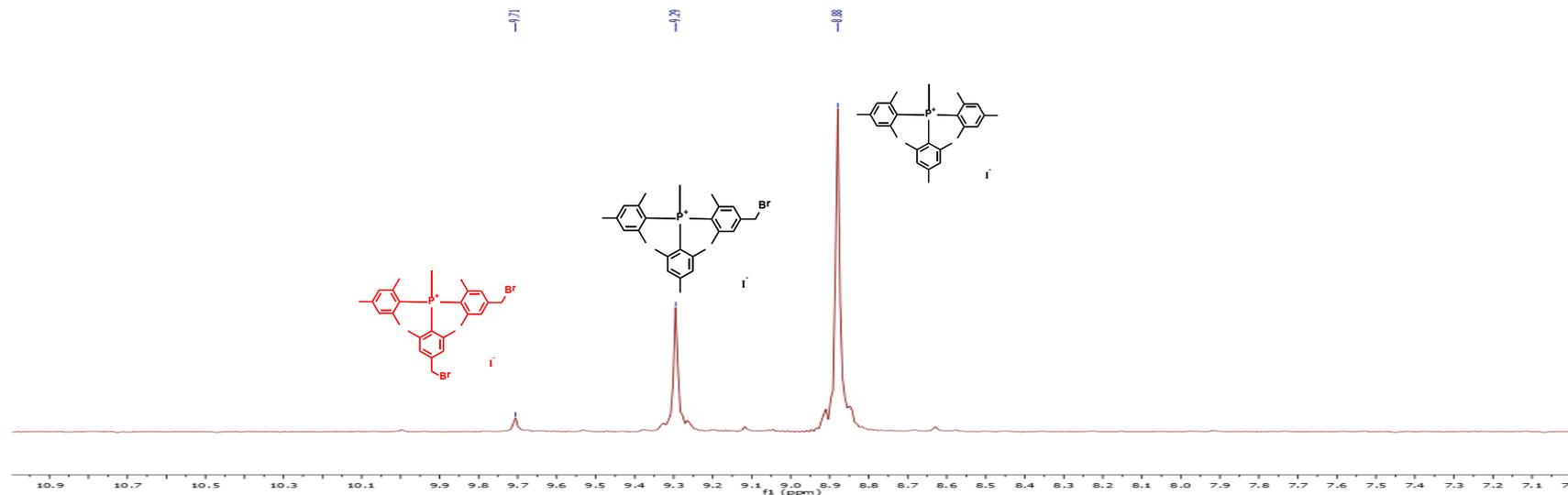
Accomplishments and Progress

Bromination of 9MeTTP⁺ cation result

³¹P NMR, DMSO solvent, enlarged of NMR in Page 12

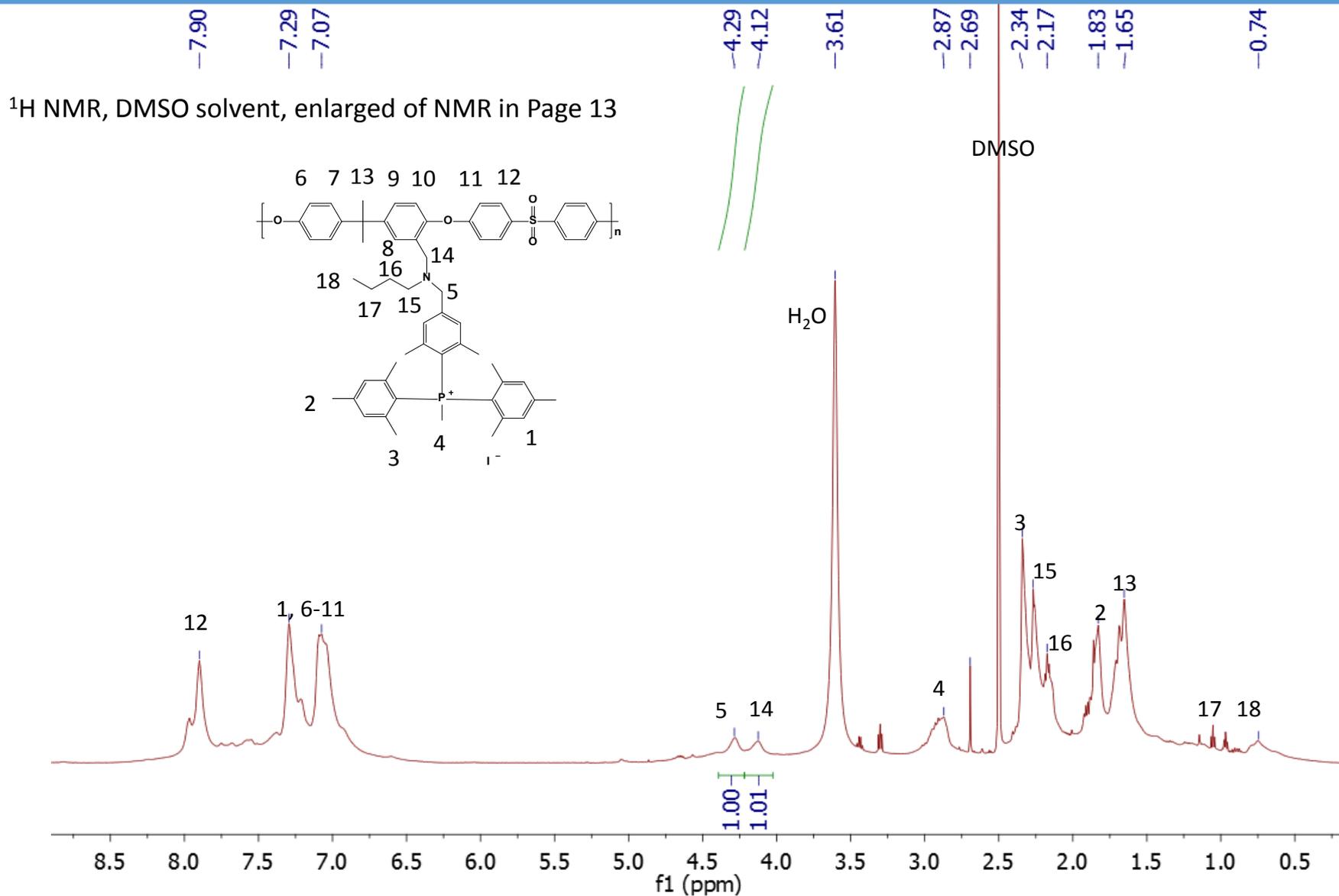


³¹P NMR, DMSO solvent



Accomplishments and Progress

9MeTTP⁺ - functionalized polymer



Accomplishments and Progress

9MeTTP⁺ - functionalized polymer

IR of CMPSf, BAPSf, Br9MeTTPf, and 9MeTTPPSf, full spectrum of IR in page 13

1700 cm⁻¹ P-Ar stretching

1670 cm⁻¹ P-Ar stretching

