

Stable Alkaline Membrane Based on Proazaphosphatranes Organic Super Base



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Project ID: FC179

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Overview

Timeline

Project started: Jan. 2018
Project end date: Dec. 2018
Percent complete: 30%

Budget

Total project funding
-DOE share: \$150K, 100%
FY18 funding \$150K

Barriers Addressed

Performance:
Low membrane conductivities
Life:
Poor membrane durability
Cost:
High cost of PGM catalyst

Partners

LBNL
Adam Weber
Daniel Miller

Relevance

Objectives: Develop new alkaline membranes with superb stability and performance to enable PGM-free alkaline membrane based fuel cell. Perform proof-of-concept work on a new class of ultra-stable and high pH proazaphosphatranes super bases for application in alkaline membranes. The ultimate goal is to develop high performance alkaline membranes and fuel cell system that rivals the performance of current Nafion membrane and PEM fuel cell system.

Milestones/Measures

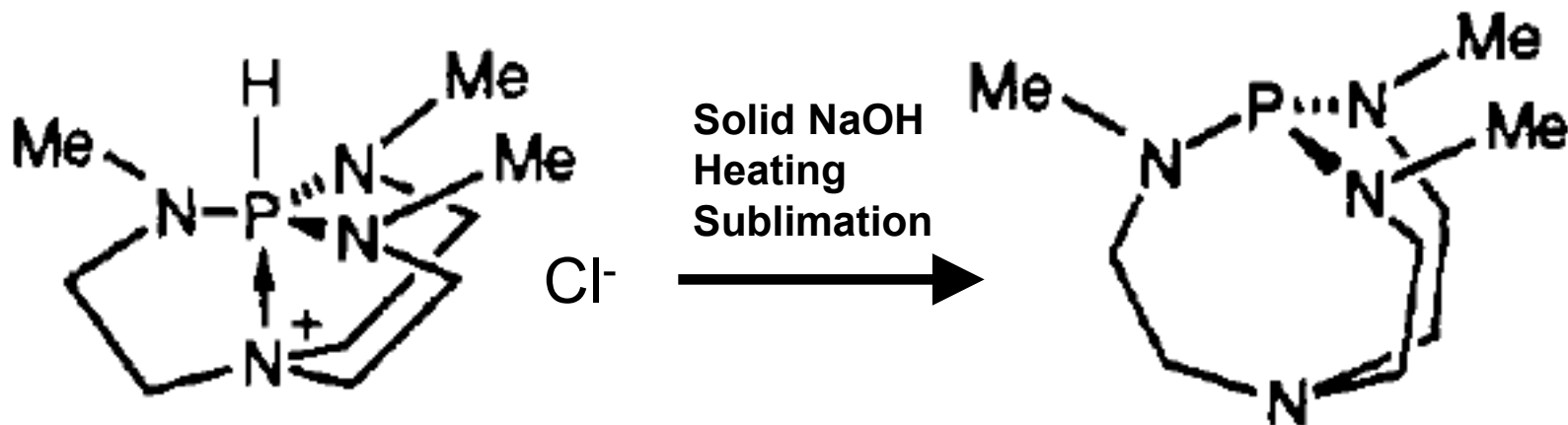
1. Synthesize crosslinking functional group tethered super base (Q1)
2. Study the stability of the polymer matrix (Q2)
3. Graft the proazaphosphatrane super base on the polymer matrixes (Q3)
4. Characterize membrane performances (go-no-go as stated in the targets) (Q4)

Targets for this proof-of-concept project

- Initial conductivity should be >100 mS/cm, better than the quats hydroxyl system.
- Membrane stability should beyond 2000 hours of MEA operation with less than 20% performance degradation.
- Initial performance in a H_2/O_2 fuel cell similar to KOH based system (film at $40\ \mu\text{m}$) at 50°C yielding $i = 620\ \text{mA/cm}^2$ at $V_{\text{cell}} = 0.60\ \text{V}$)

Accomplishments and Progress

The ultra-stability of proazaphosphatranes organic super base



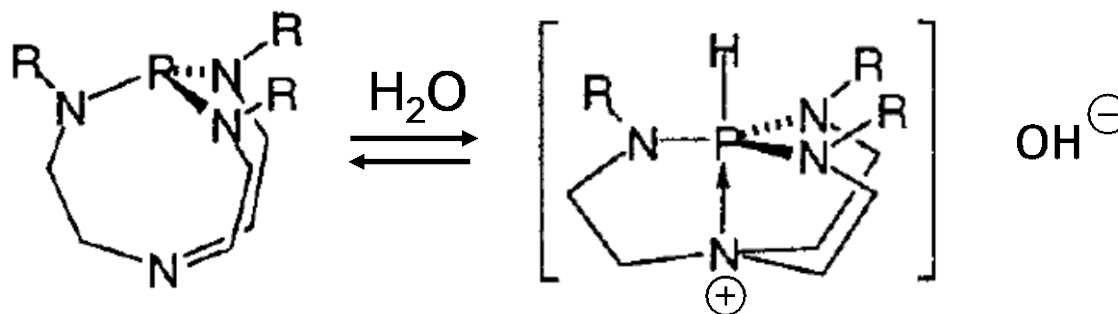
Slowly heating the starting materials with a large excess of anhydrous NaOH to 200°C under vacuum over a period of several hours gave no indication of reaction. Above 200°C, a sudden sublimation of end product from the reaction mixture is observed. These testify to the superb stability and basicity of the proazaphosphatranes organic super base.

C. Lensink, S. K. Xi, L. M. Daniels, and J. G. Verkade, J. Am. Chem. Soc. 1989, 111, 3478-3479

Accomplishments and Progress (cont.)

High alkalinity of the superb base in water

Proazaphosphatranes organic super base and its transformation into hydroxide base in aqueous solution. The pH of 1M solution is around 14, qualifying it for strong base in aqueous solution. Coupled with the superb thermal stability, it is the ideal choice to be used as base functional groups in OH⁻ conducting membrane.



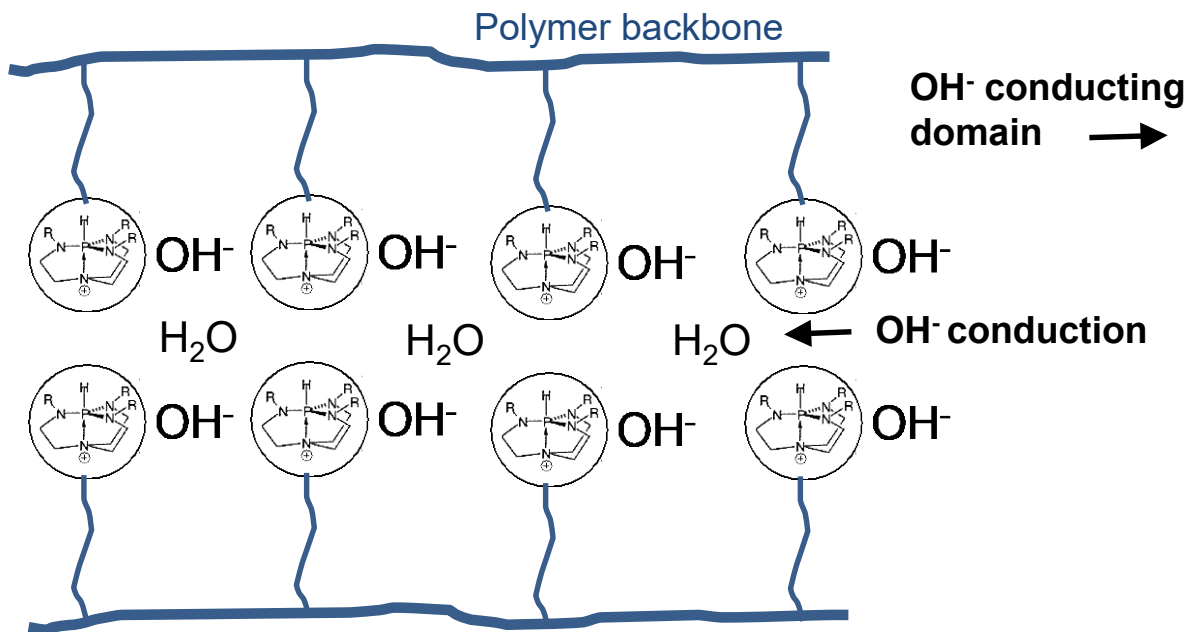
R = Me, *i*-Pr, etc.

The R groups can be synthetically changed into different alkyl structures.

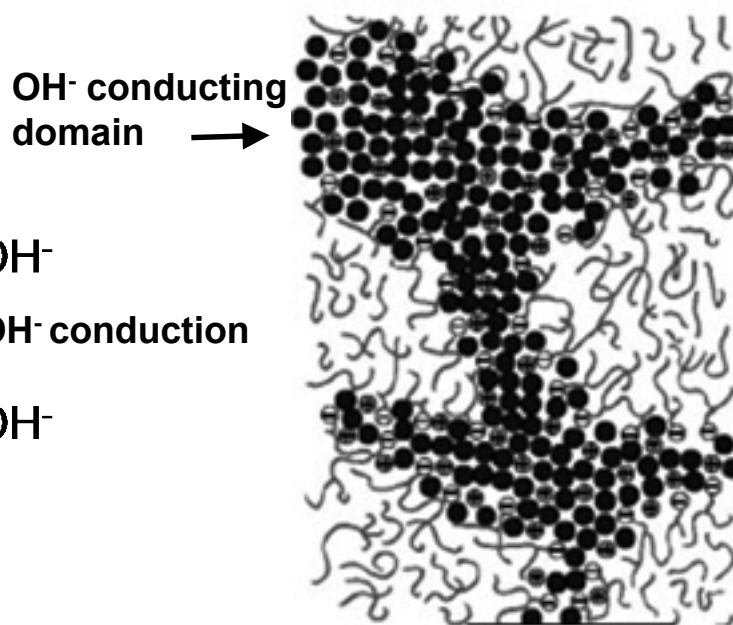
Accomplishments and Progress (cont.)

Membrane design with proazaphosphatranes super base and a stable polymer matrix

Schematic of the polymer design



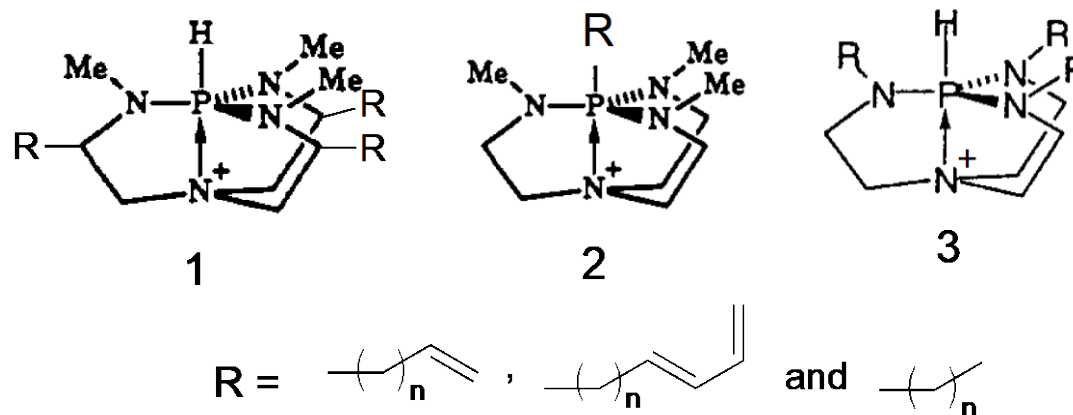
Schematic of the membrane structure



The super base units are grafted to a stable polymer matrix/backbone to achieve a high OH^- conducting polymer as shown in the polymer design. Further design the polymer matrix leads to formation of micro HO^- ion conducting channels in the membrane structure as in the Nafion.

Accomplishments and Progress (cont.)

Three types of Proazaphosphatranes with alkyl or alkene derivatives

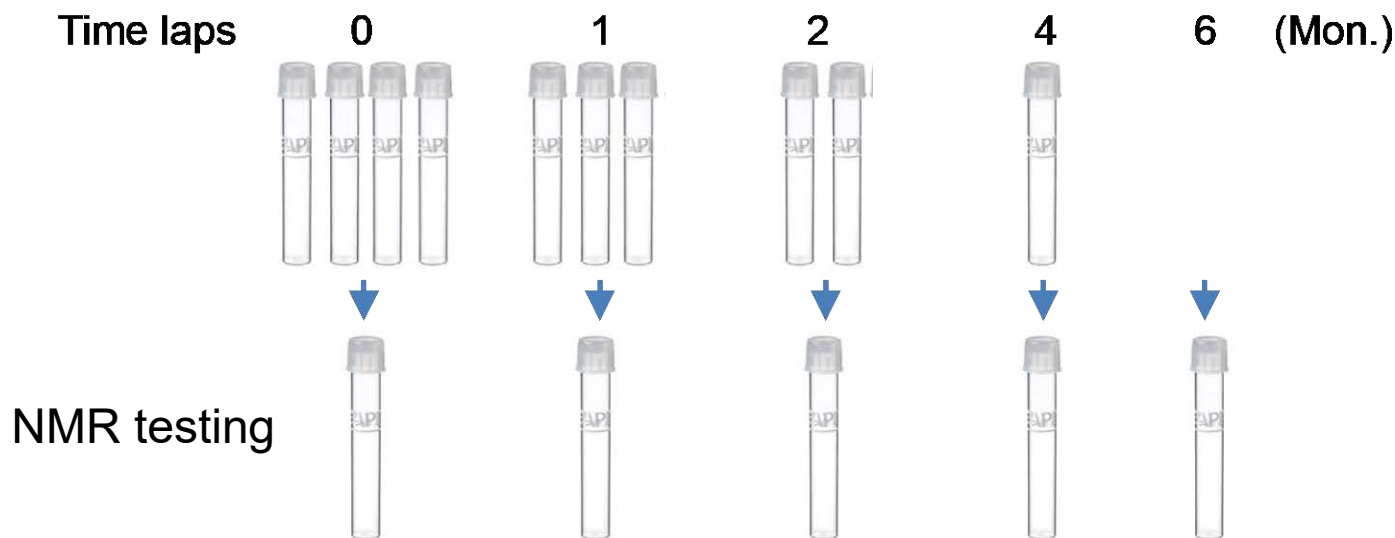
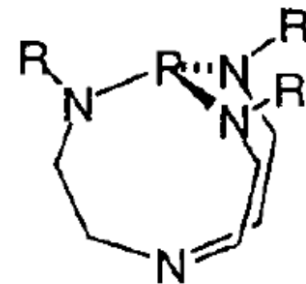


In order to graft the proazaphosphatranes base molecules onto the polymer chains, a connection site will need to be introduced to the super base. The places of R groups are the potential connection sites between the super base and the polymer backbone. However, introduction of the R groups could lead to new reaction sites that can be potentially a degradation point during membrane operation. Therefore, the chemical stability of the super base and its derivatives is further investigated.

Accomplishments and Progress (cont.)

Stability study of Proazaphosphatranes and its derivatives

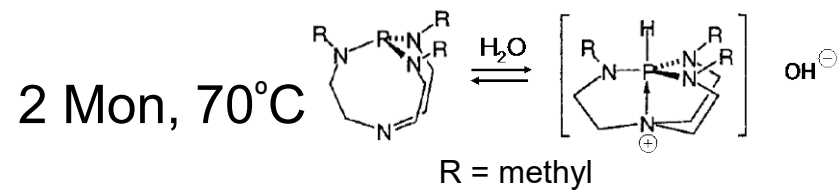
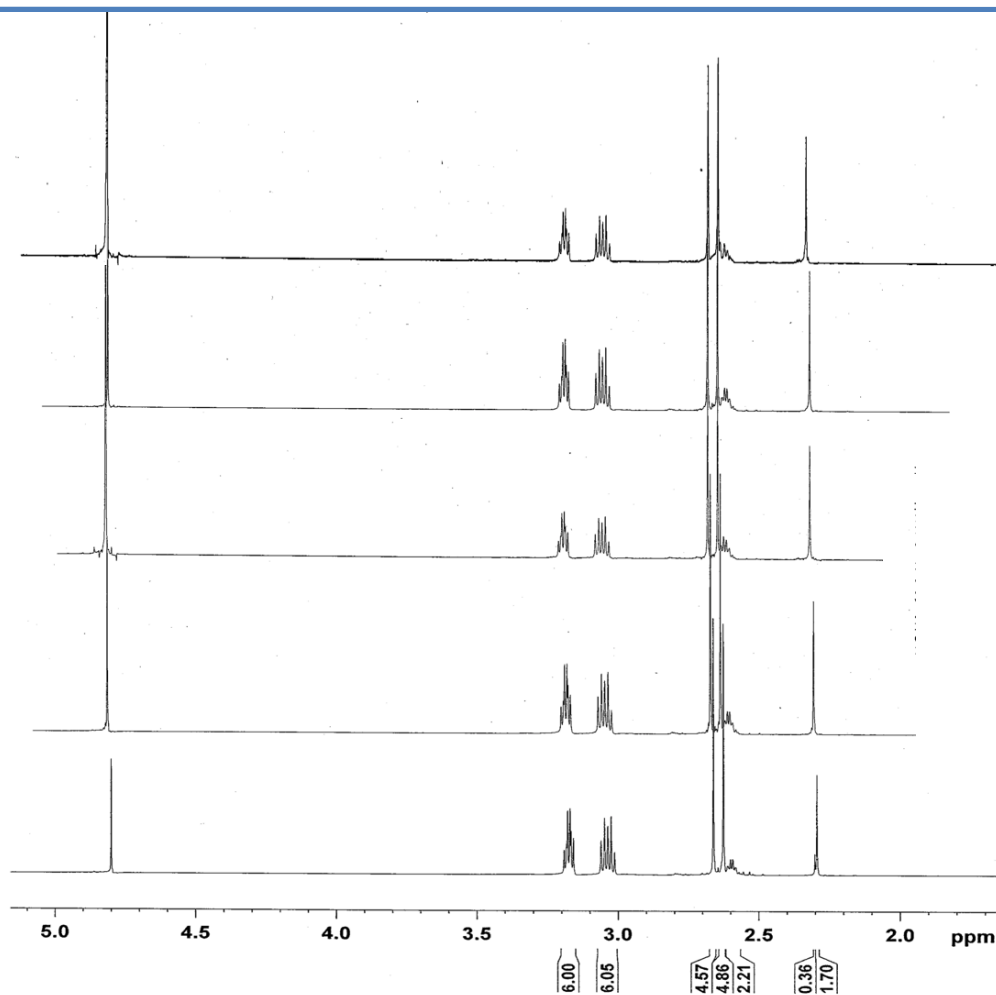
The super bases are made into 0.1M D₂O solution, and aged at a given temperature in sealed plastic tubes to investigate their stability in a six-months period. Both 25°C and 70°C are chosen, and two types of super base (R is methyl and isopropyl) are chosen.



Each sample, both ¹H and ¹³C NMR are performed to study the molecular structure transformation. The spectra before and after aging are compared.

Accomplishments and Progress (cont.)

Stability study of Proazaphosphatranes and its derivatives

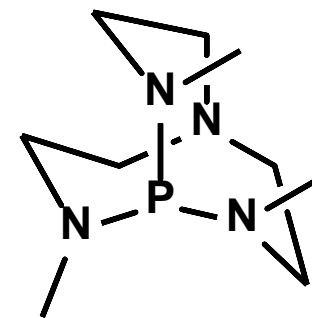


2 Mon, 25°C

1 Mon, 70°C

1 Mon, 25°C

T₀, 25°C

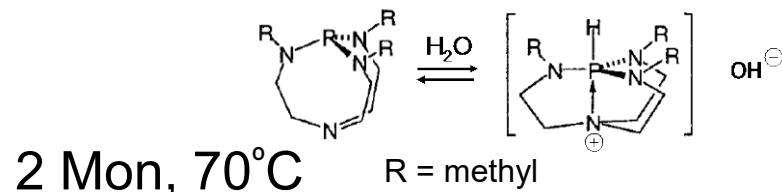
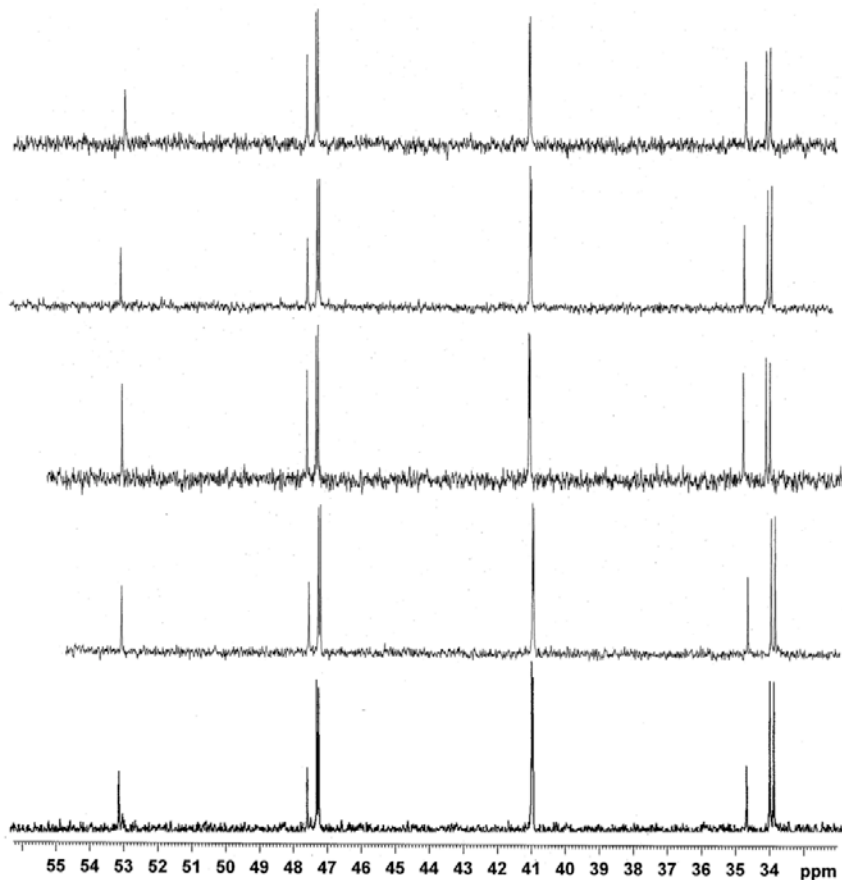


The NMR spectrum changes very little after 2 months aging at 70°C.
The methyl functionalized super base is stable.

Accomplishments and Progress (cont.)

Stability study of Proazaphosphatranes and its derivatives

^{13}C NMR

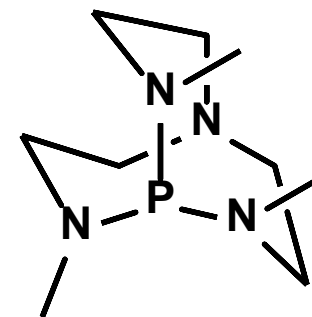


2 Mon, 25°C

1 Mon, 70°C

1 Mon, 25°C

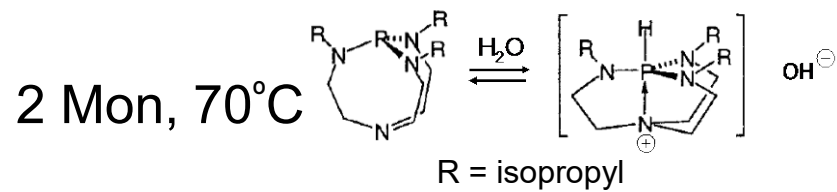
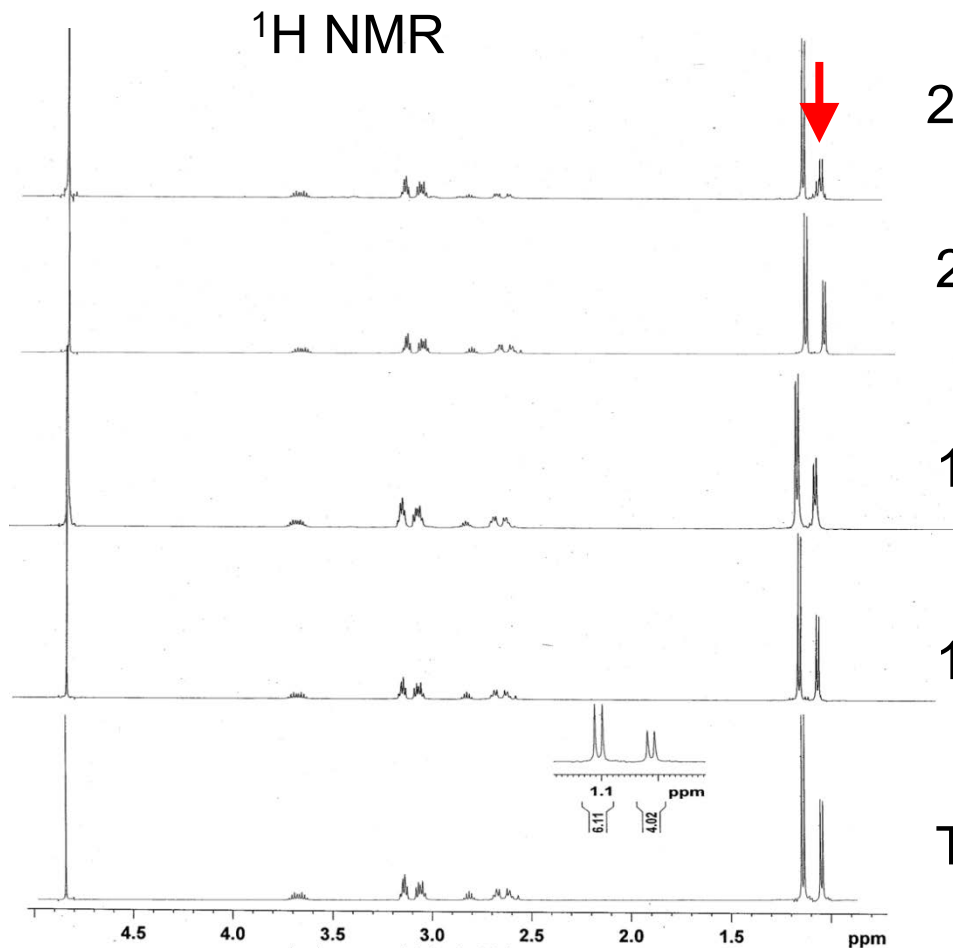
T_0 , 25°C



The NMR spectra change very little after 2 months aging at 70°C.
The methyl functionalized super base is stable.

Accomplishments and Progress (cont.)

Stability study of Proazaphosphatranes and its derivatives

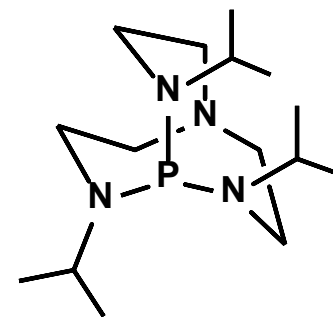


2 Mon, 25°C

1 Mon, 70°C

1 Mon, 25°C

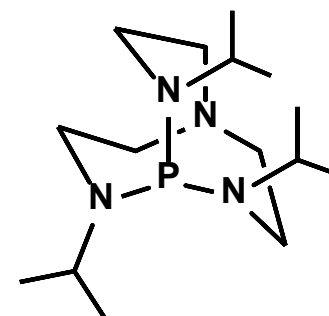
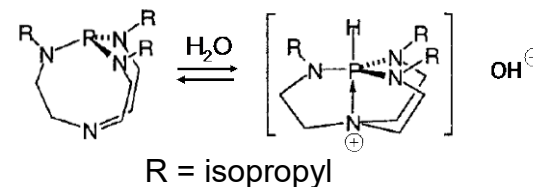
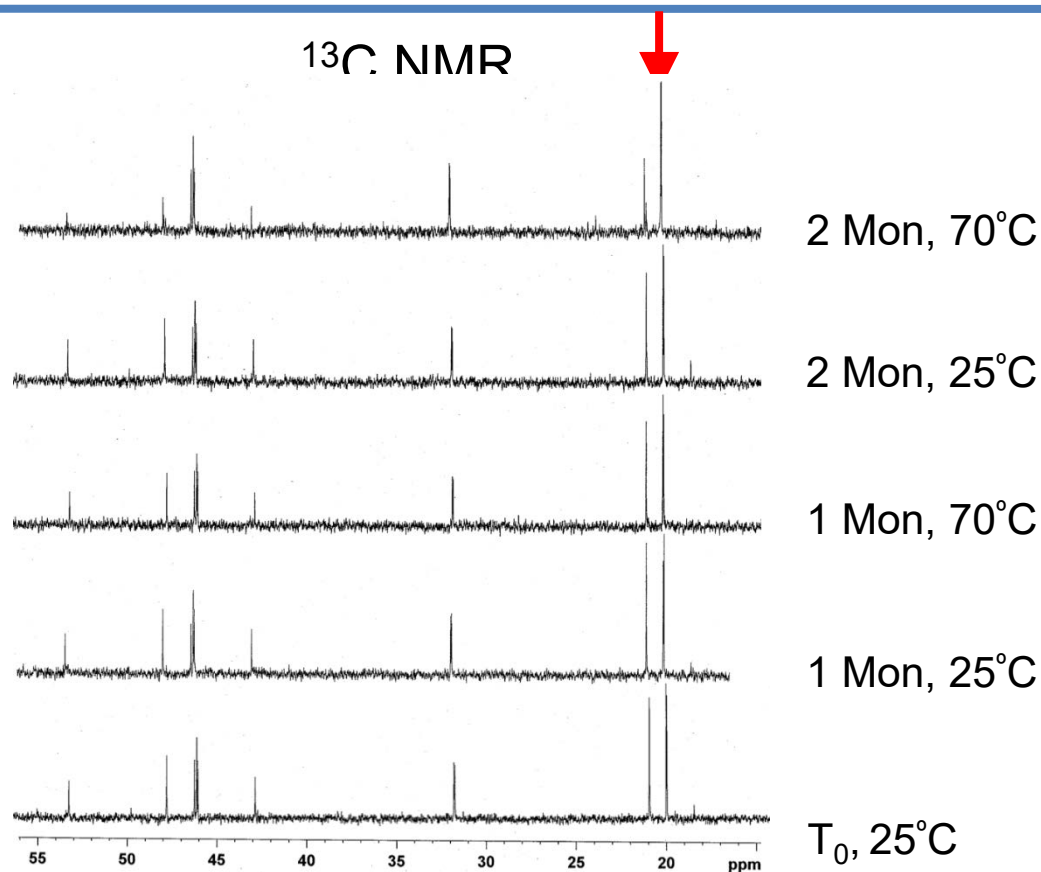
T₀, 25°C



The NMR spectra change at the isopropyl site after 2 months aging at 70°C. The isopropyl functionalized super base is **NOT** stable.

Accomplishments and Progress (cont.)

Stability study of Proazaphosphatranes and its derivatives

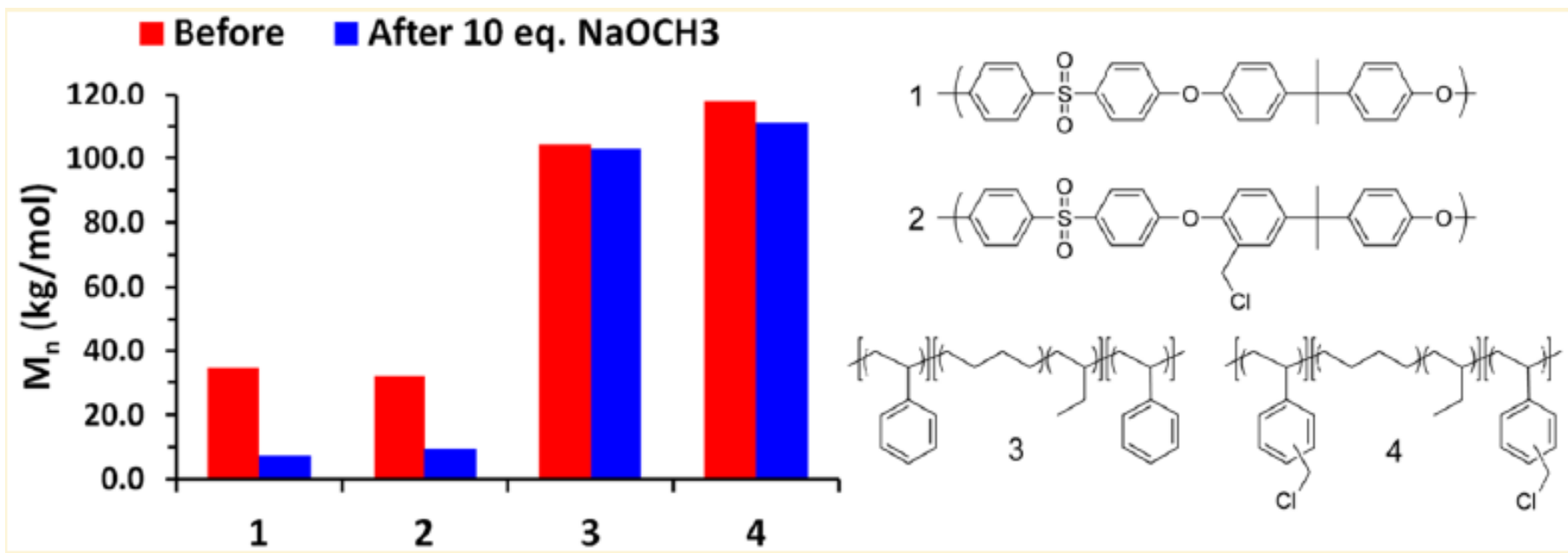


The NMR spectra change at the isopropyl site after 2 months aging at 70°C. The isopropyl functionalized super base is **NOT** stable. Therefore, the 2, 2', 2'' connections may not be used to form bonding with the polymer matrix.

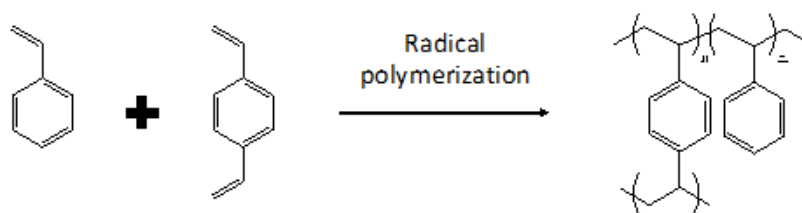
Accomplishments and Progress (cont.)

Identification of a stable polymer matrix

Polystyrene-based copolymers exhibit base stability



Proposed all hydrocarbon polymer backbone



Macromolecules 2016, 49, 3361–3372

Collaboration & Coordination

This project is a collaboration among three teams at LBNL.

1. Gao Liu's team: Proazaphosphatranes stability investigation, and derivative synthesis, and membrane integration.
2. Daniel Miller's team: Member development and integration and stability study.
3. Adam Weber's team: AEM development and testing, and water management investigation and modeling.

Remaining Challenges and Barriers

Although the proazaphosphatranes super base itself is very stable, the addition of alkyl connection tends to introduce unstable sites for degradation as we demonstrated in the case of propyl substituted super base.

Proposed Future Work

1. Continue the stability investigation of the super base and its derivatives.
2. Stability investigation of the polymer matrix in alkaline condition.
3. Identify the stable connections between the super base and polymer matrix.
4. Accomplish the super base polymer development.
5. Finish all the tasks and milestones.

Any proposed future work is subject to change based on funding levels

Summary

1. Identified a class of alkaline organic bases – proazaphosphatranes, which is ultra stable at high pH conditions.
2. Identified a class of polymer matrix, that are stable at high alkaline conditions.
3. Demonstrated possible degradation sites of the super base derivatives, and Identified the stable structures of the proazaphosphatranes super base.