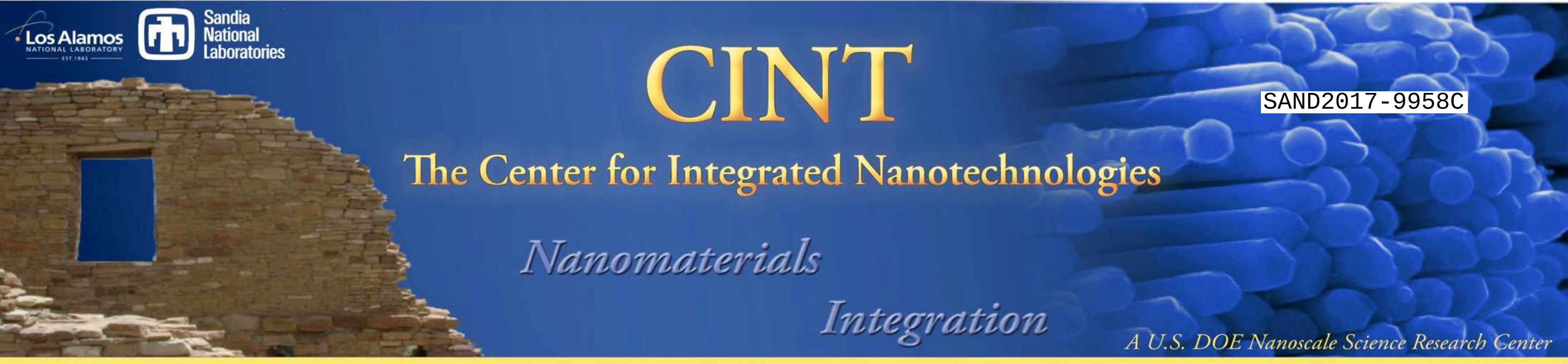


SAND2017-9958C

Dynamic Membrane Materials from Amphiphilic Block Copolymers

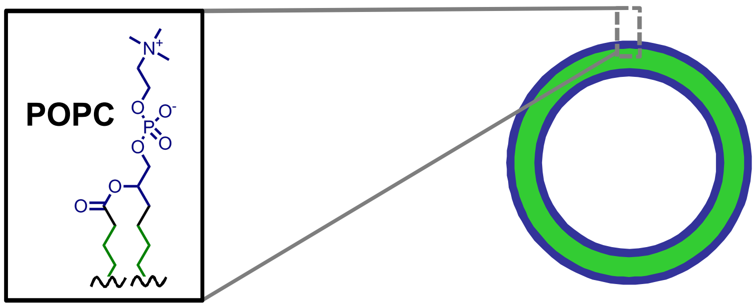
Walter F. Paxton

Center for Integrated Nanotechnologies / Sandia National Laboratories

This work was performed in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science (project number 2016AU0018). Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

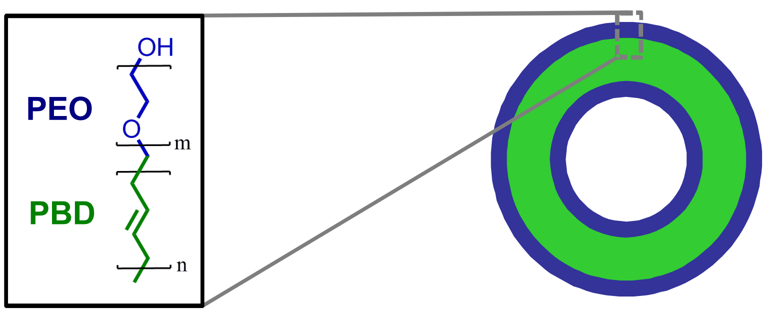
Mimicking Biological Membranes

Liposomes



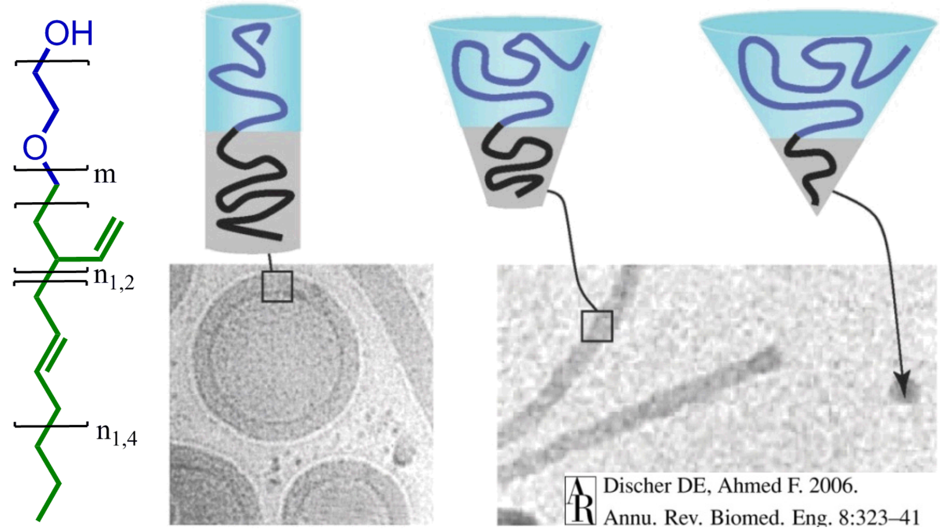
2 Major Challenges:
Limited Chemical and Mechanical Stability
Limited Modification Chemistries

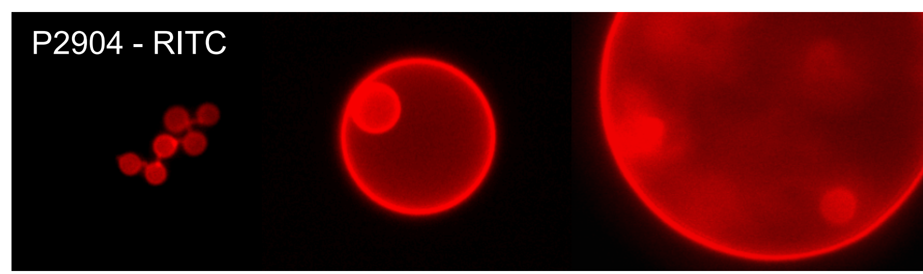
Polymersomes



Polymersomes Can Help
Enhanced Chemical and Mechanical Stability
Unlimited Modification Chemistries

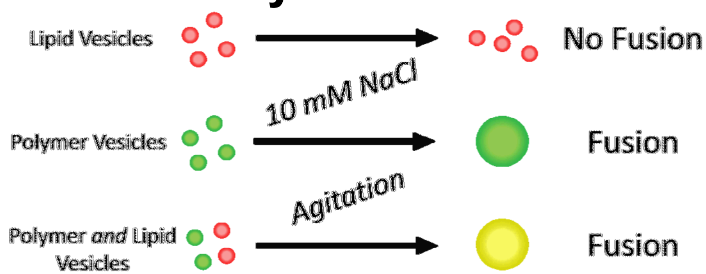
Can we incorporate or mimic **properties** and **functions** of biological cells to create robust **advanced materials**?





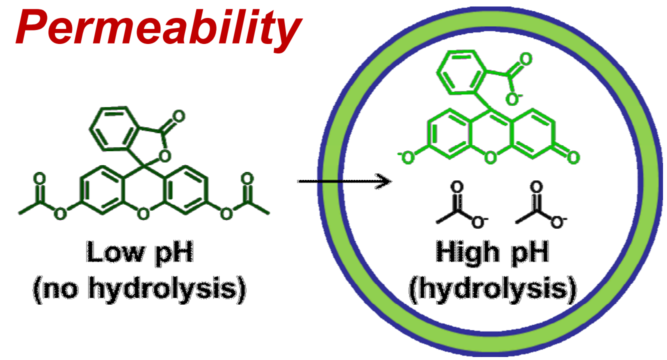
Dynamic Polymer Vesicle Membranes

Mechanically-Activated *Fusion*



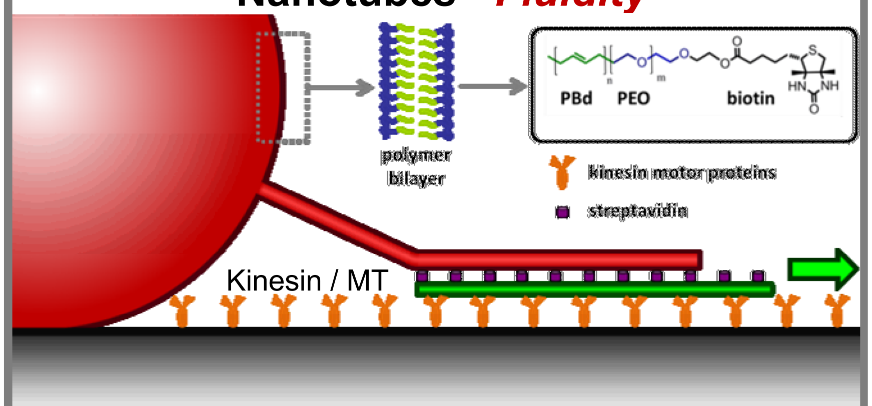
Angew. Chem. – Int. Ed. **2014,** *53,* 3372-3376; *J. Poly. Sci. B,* **2014,** *53,* 297–303

Lysosome-Mimicking Vesicles *Permeability*



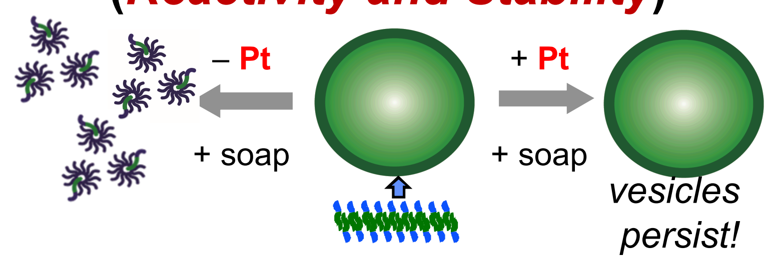
Soft Matter **2013,** *9,* 11295–11302

Dynamic Assembly of Polymer Nanotubes - *Fluidity*



Nanoscale, **2015,** *7,* 10998–11004

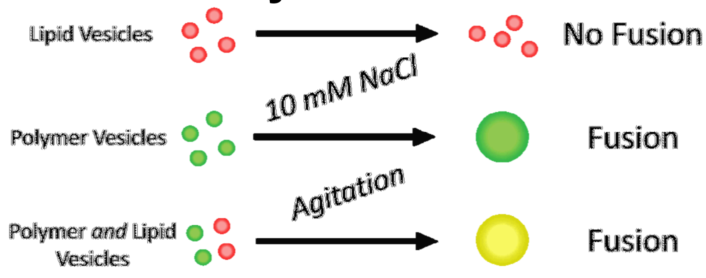
Catalytically-Active Cross-Links (*Reactivity and Stability*)



Chem. Mater., **2015,** *27, 4808–4813*

Dynamic Polymer Vesicle Membranes

Mechanically-Activated *Fusion*

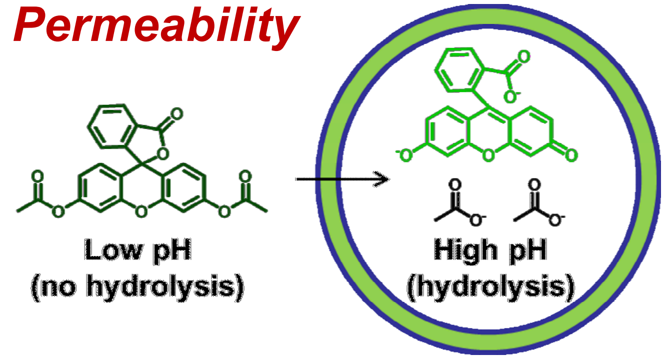


I. M. Henderson, W. F. Paxton, *Angew. Chem. – Int. Ed.* ***2014,*** *53,* 3372-3376; *J. Poly. Sci. B,* **2014,** *53,* 297–303

Dynamic Polymer Vesicle Membranes

Lysosome-Mimicking Vesicles

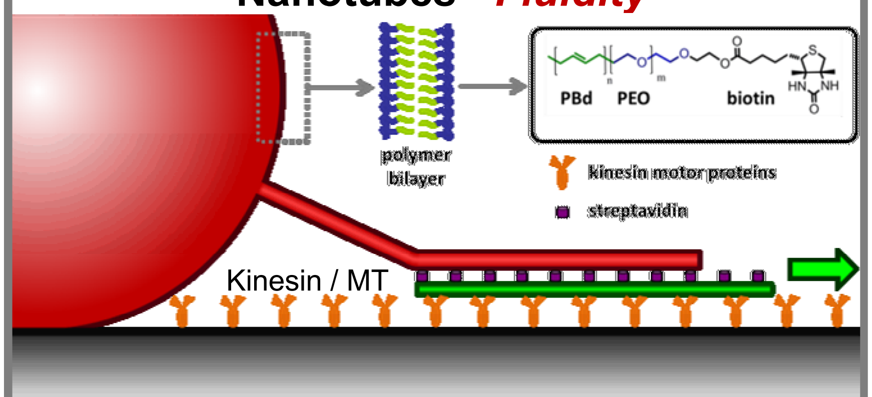
Permeability



W. F. Paxton et al. *Soft Matter* **2013,** *9,* 11295–11302

Dynamic Polymer Vesicle Membranes

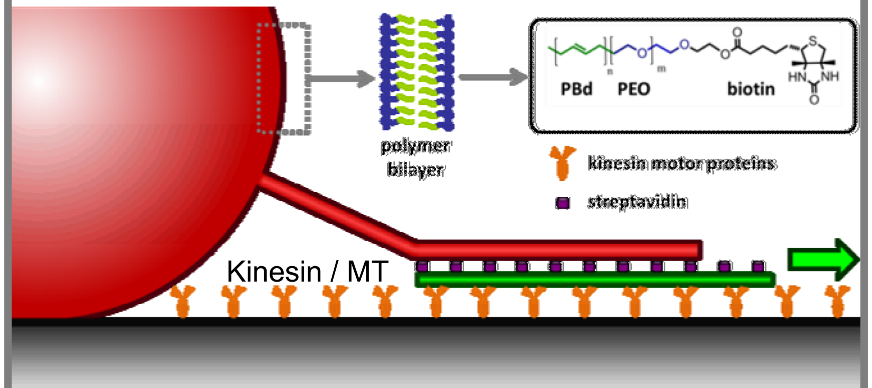
Dynamic Assembly of Polymer Nanotubes - *Fluidity*



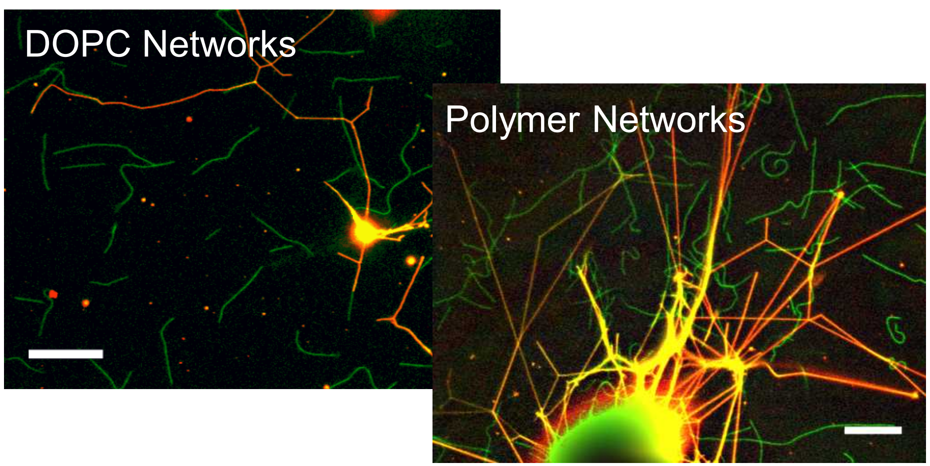
W. F. Paxton et al. *Nanoscale,* **2015,** *7,* 10998–11004

Fluidity in Polymer Membrane Nanotubes

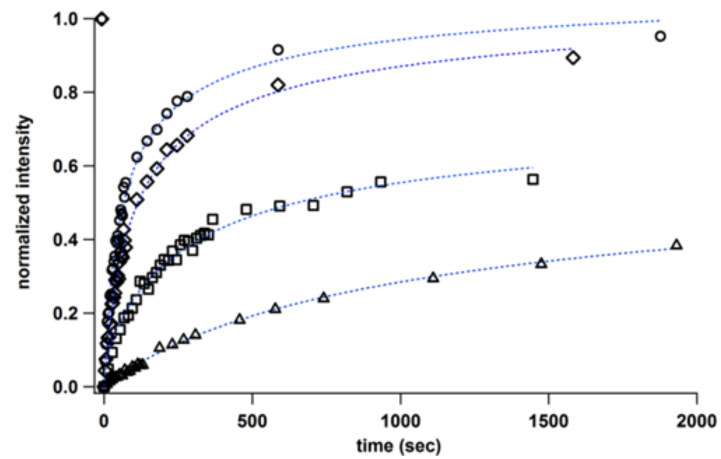
Dynamic Assembly of Polymer Nanotubes



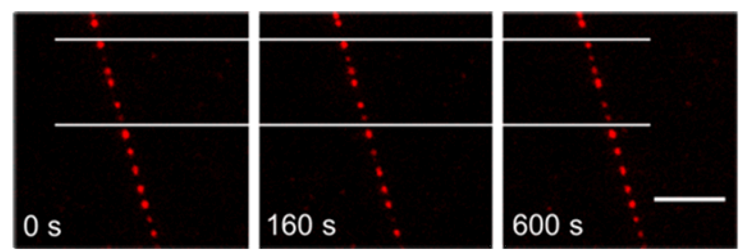
W. F. Paxton et al. *Nanoscale,* **2015,** *7,* 10998–11004



FRAP in Polymer Nanotubes



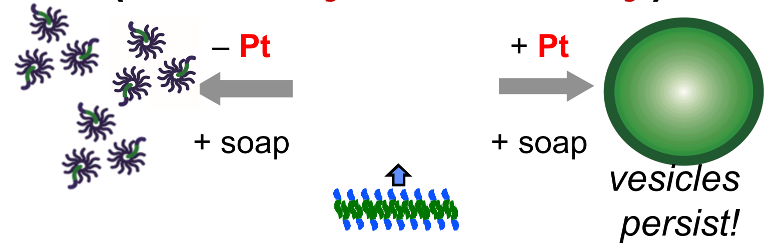
Fluidity of Adsorbed Quantum Dots



*No fluidity in polymer nanotubes either…**WHY?***

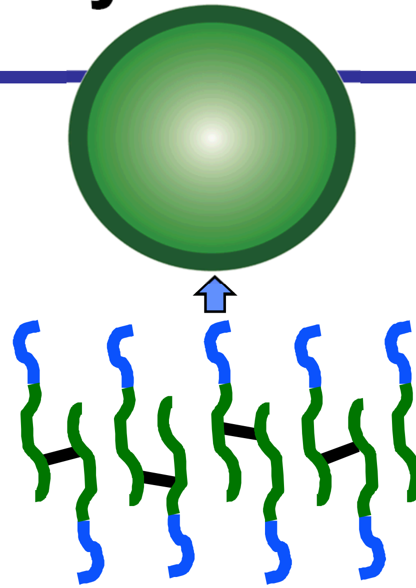
Dynamic Polymer Vesicle Membranes

Catalytically-Active Cross-Links
(*Reactivity and Stability*)

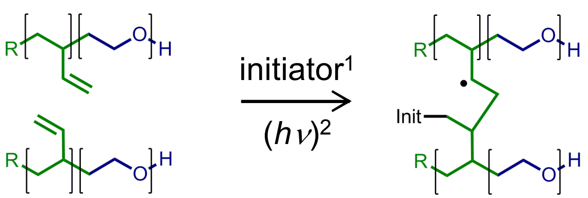


W. F. Paxton et al. *Chem. Mater,* **2015,** *27, 4808–4813*

ROBUST Polymer Vesicles Membranes

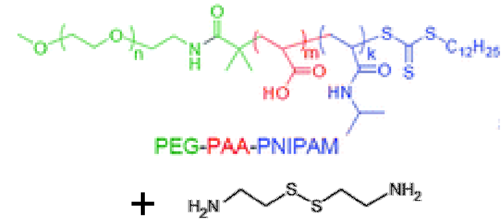


Radical cross-linking



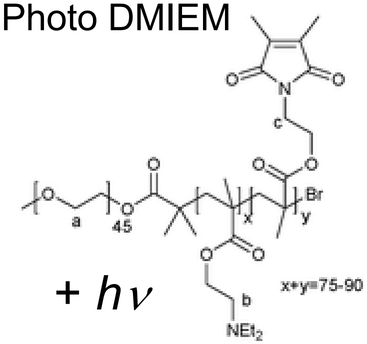
1. Discher et al. *JPCB* **2002,** *106,* 2848.
2. Jofre et al. *JPCB* **2007,** *111,* 5162.

Amide coupling…



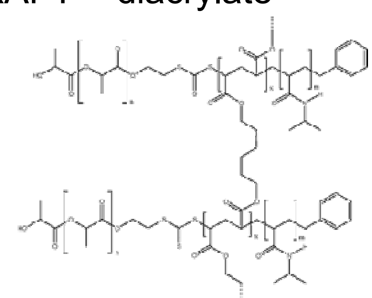
Zhiyuan Zhong et al. *J. Mater. Chem.*, **2011,** *21,* 19013.

Photo DMIEM



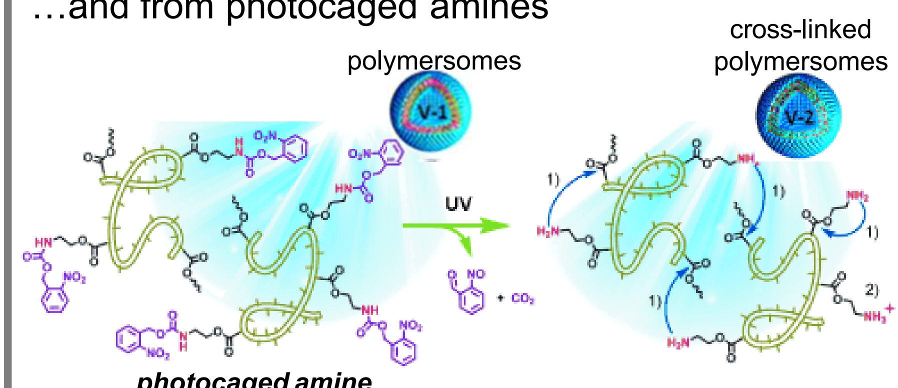
Voit et al. *Chem. Commun.* **2011,** *47,* 3466-3468.

RAFT + diacrylate



Stenzel et al. *Langmuir* **2004,** *20,* 10809-10817

…and from photocaged amines

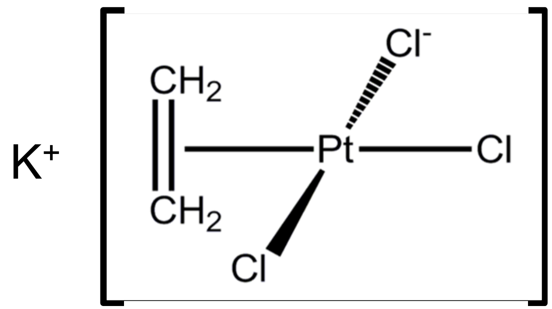


Shiyong Liu et al. *Angew. Chem.* **2014,** *53,* 3138.

Covalent X-links are ROBUST but, limited control over DYNAMICS

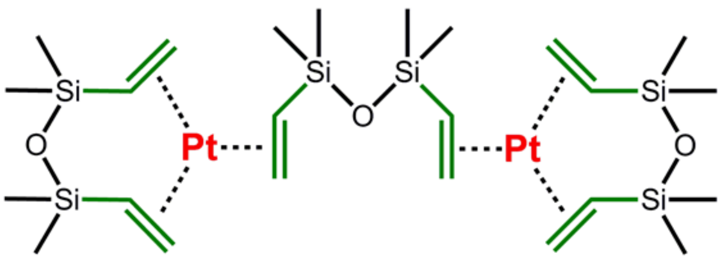
Platinum-Alkene Complexes

Zeise's Salt



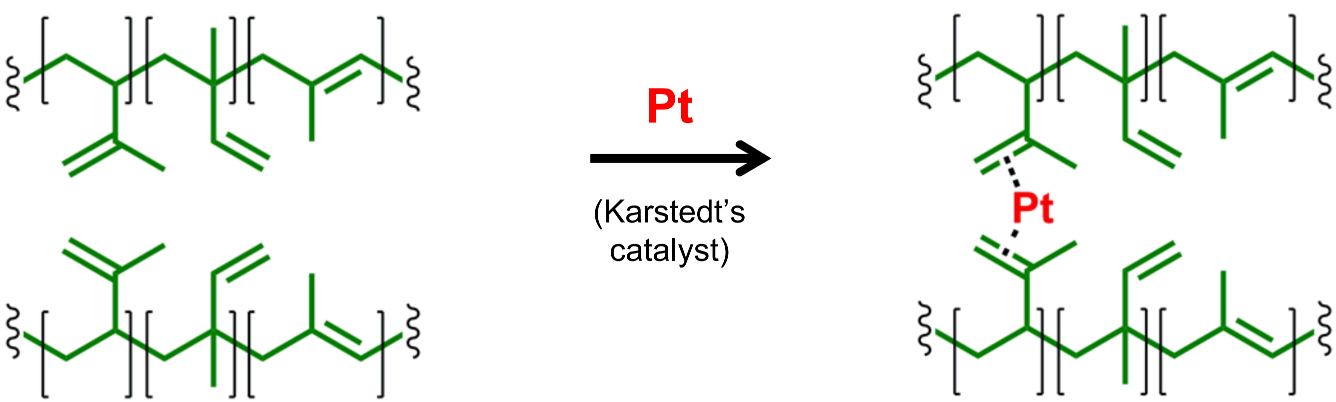
η^2-alkene compound (1831)

Karstedt's Catalyst

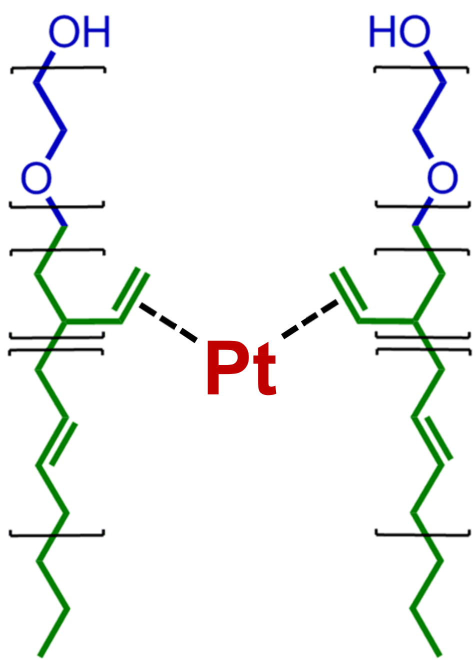


η^2-alkene compound (1973)
hydrosilylation catalyst

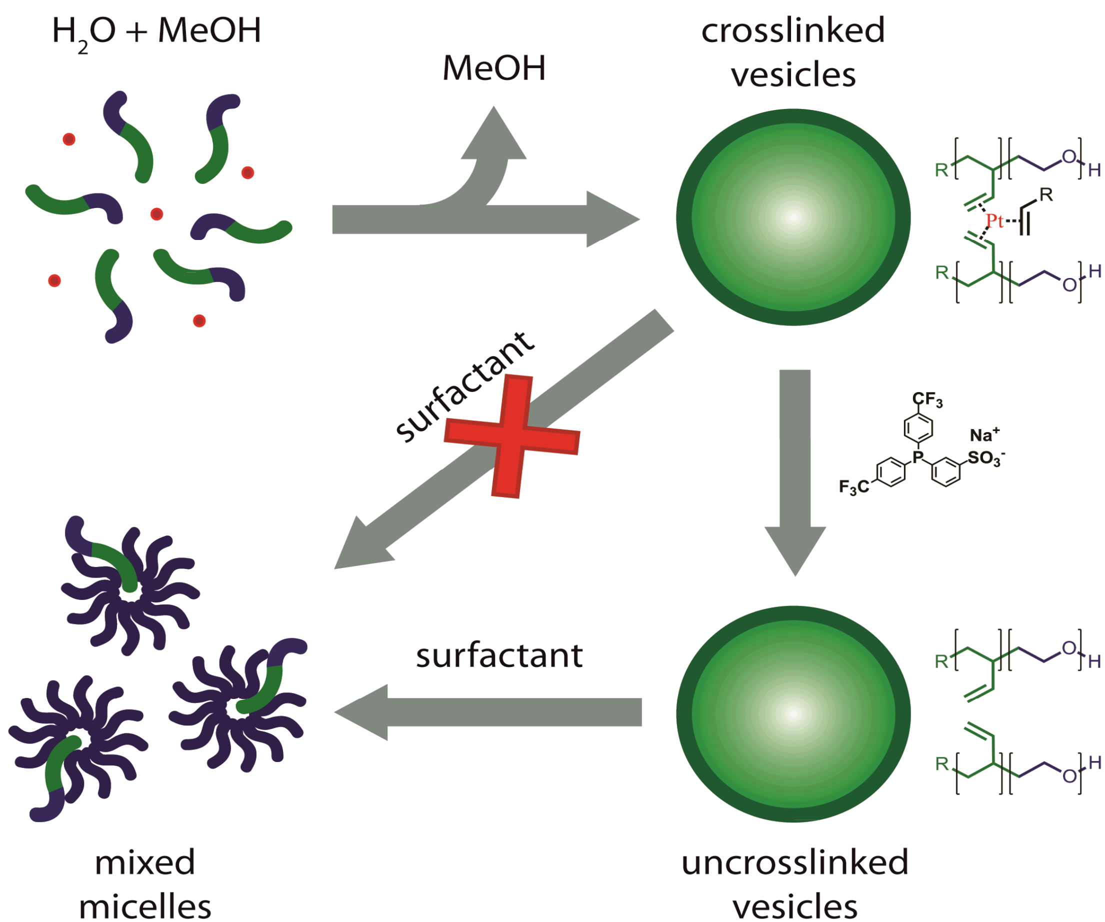
Isoprene–Pt(0) Coordination (Rupar et al. *JACS*, **2011**)



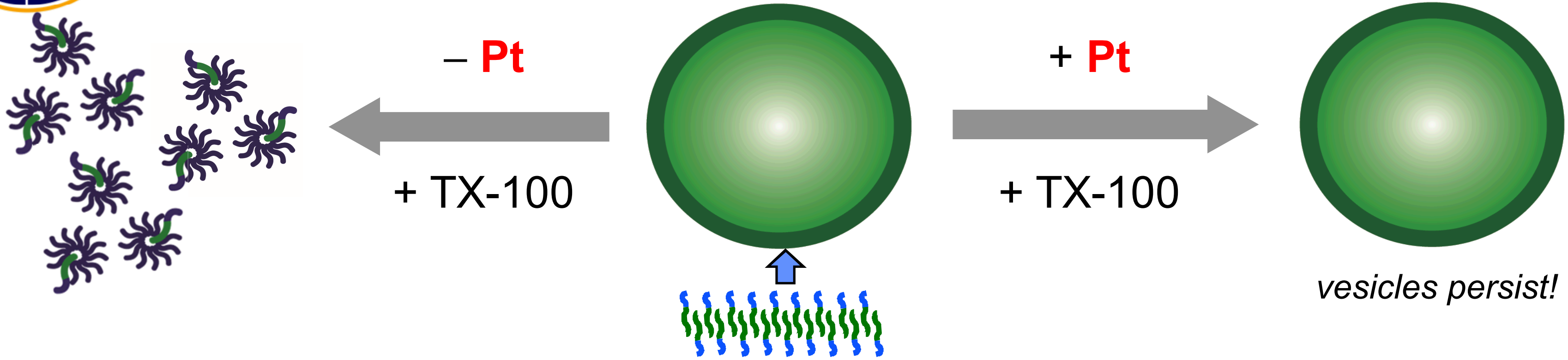
Capable Crosslinks: Polymersomes Reinforced with Catalytically Active Metal-Ligand Bonds

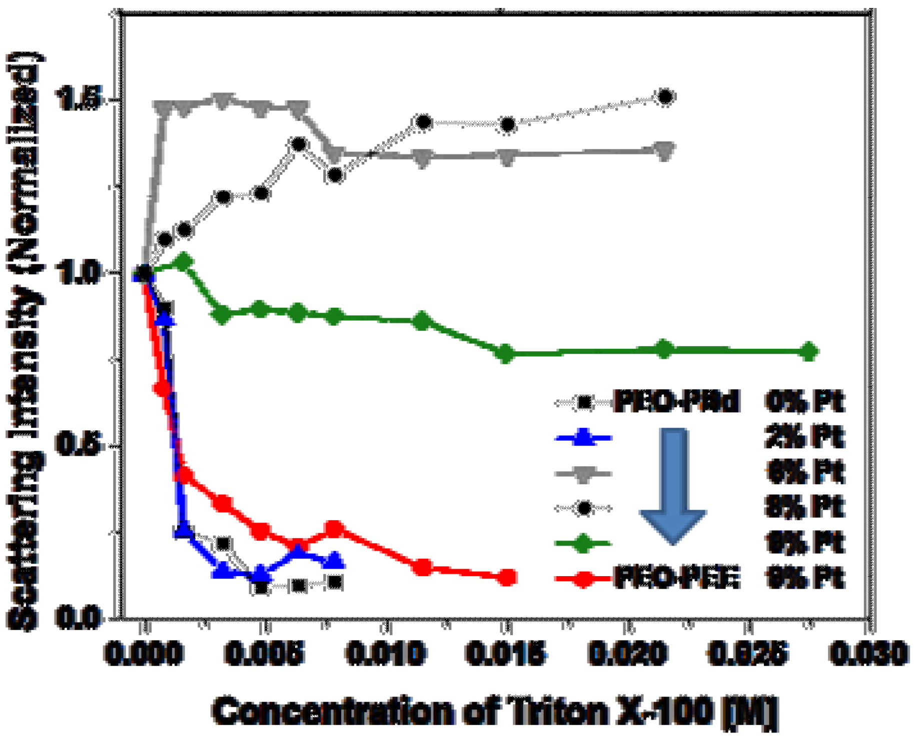


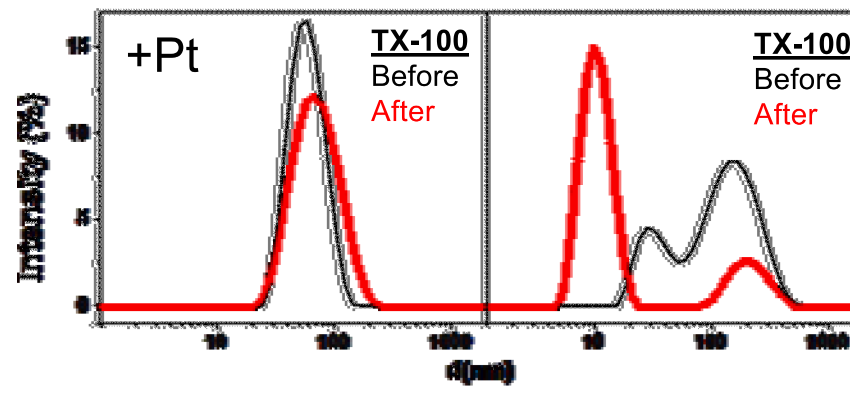
Exploit organometallic interactions to create membranes that are both ***robust*** and ***dynamic***.



Surfactant-Resistant Cross-linked Polymersomes



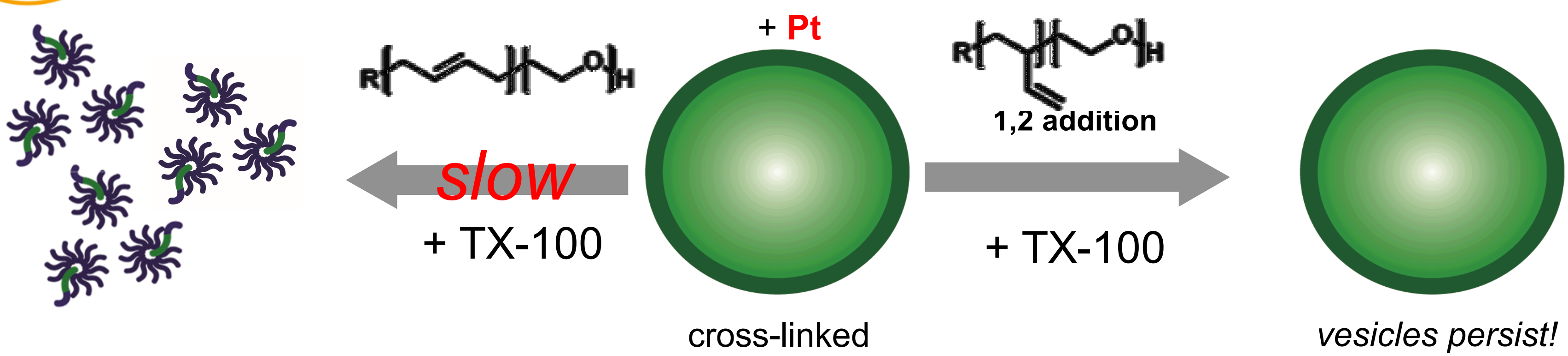


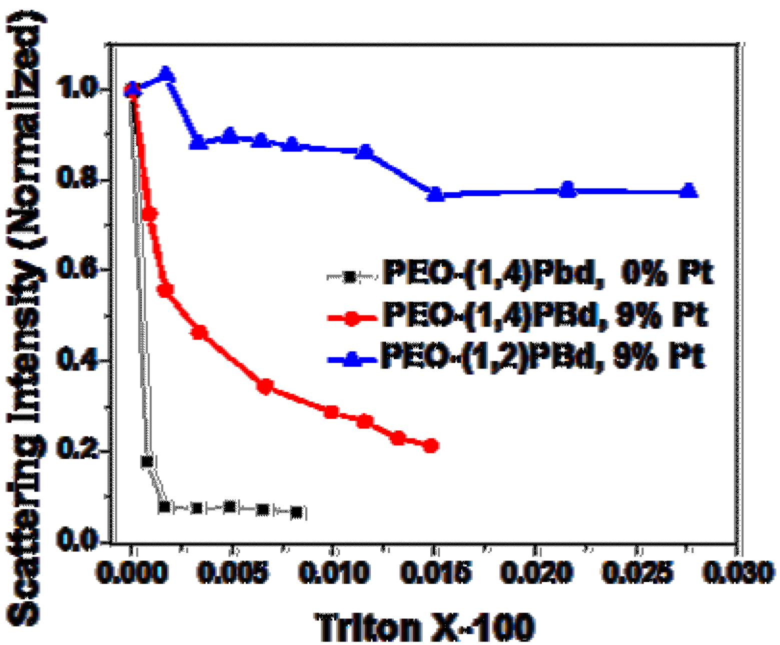


Uncross-linked vesicles → mixed micelles

Cross-linked vesicles resist surfactant

Stability of PEO-PBd--Pt: 1,2 vs. 1,4 addition





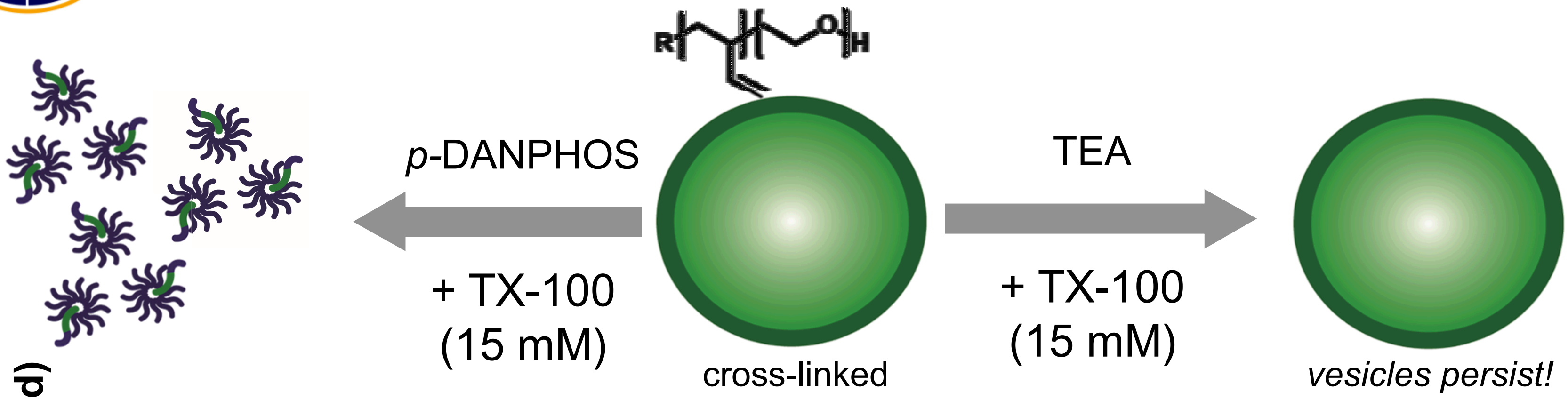
1,4 PBd is *MORE* resistant with **Pt**…

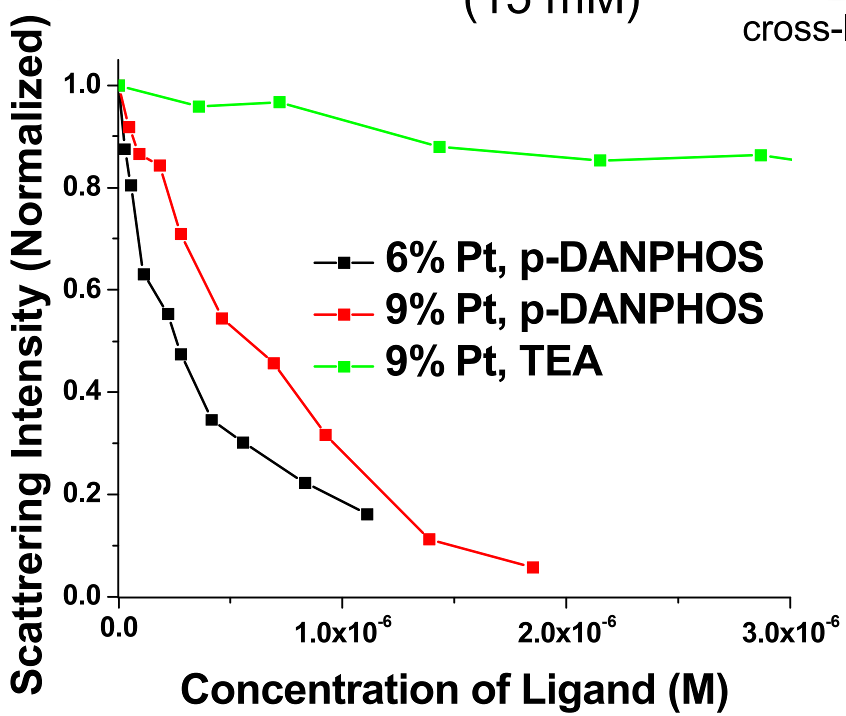
…but *LESS* resistant than 1,2 PBd

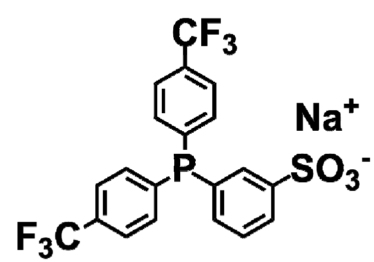
Two effects:

- Sterics: Pendant vs. main-chain
- Electronics: bond energies
  (1,2--**Pt** > 1,4--**Pt**)

Selective Reversibility w/ a Competing Ligand

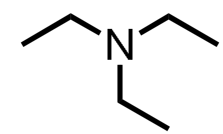






p-DANPHOS

bis(4-trifluoromethylphenyl)(3-sulfonatophenyl)phosphine

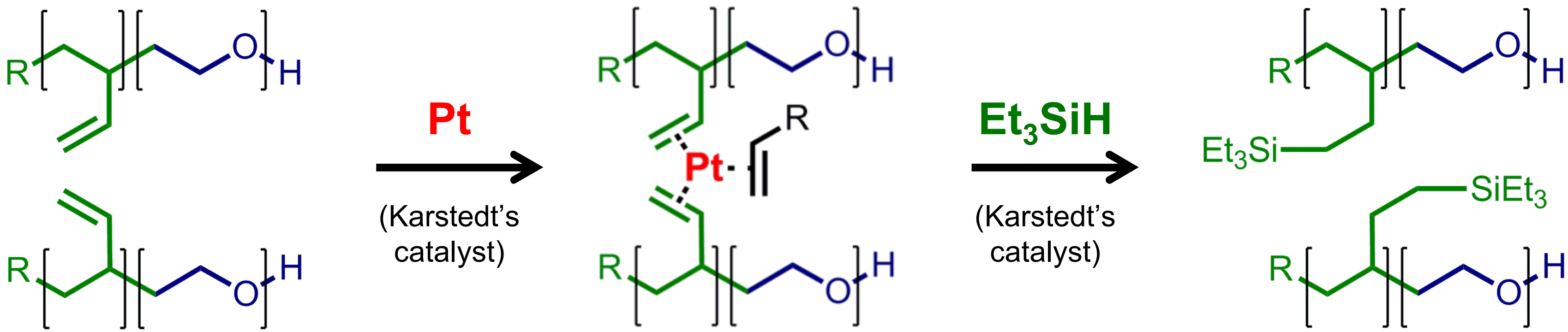


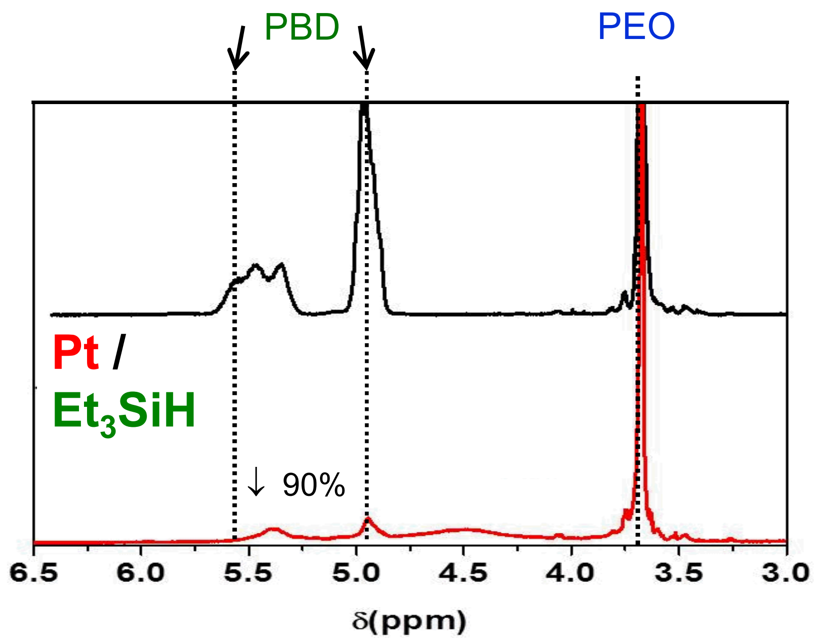
TEA

triethylamine

Reversible/Dynamic Cross-links via Competitive ligands

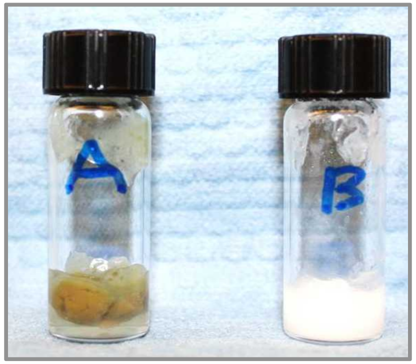
Pt in Cross-linked Polymersomes Are Catalytically Active





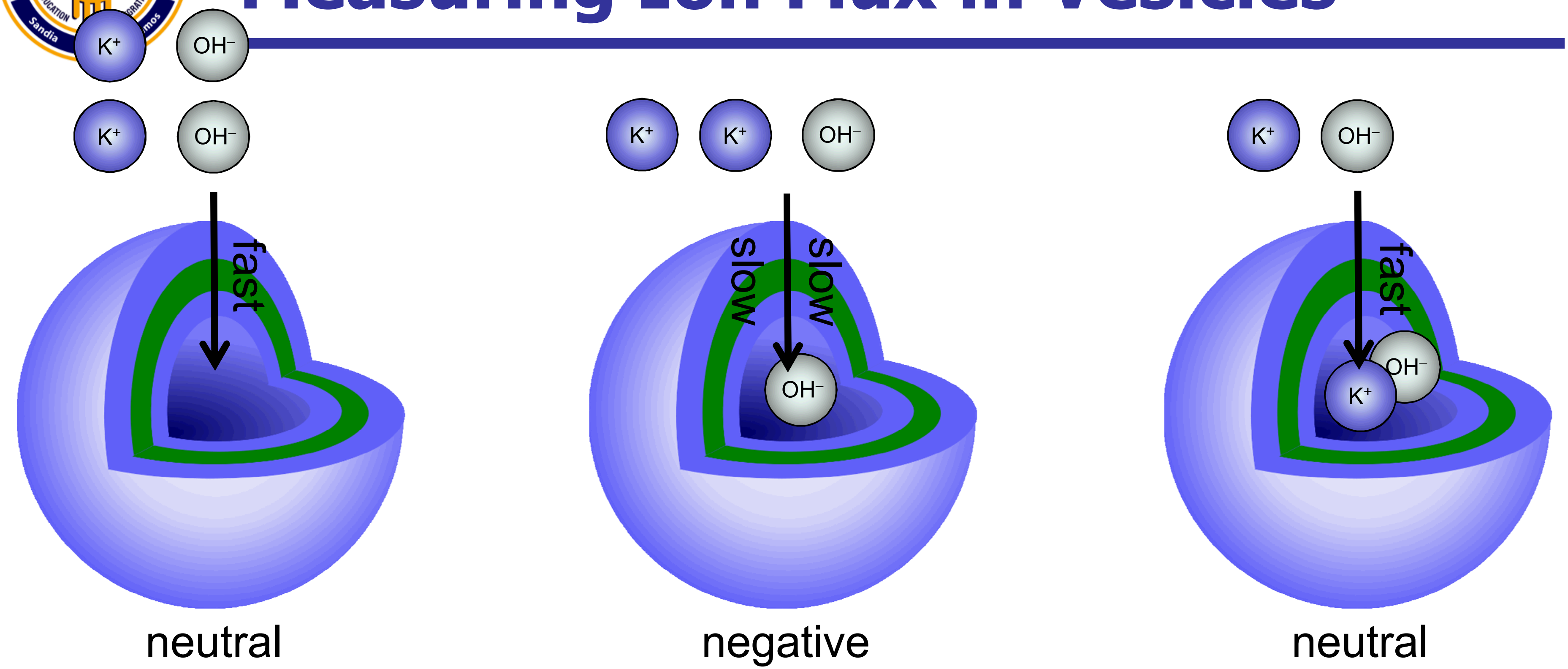
1 h Agitation:

- 90% hydrosilylation
- emulsion (both)
- color = Pt(0)↓



Catalytically-Active Cross-links

Measuring Ion Flux in Vesicles

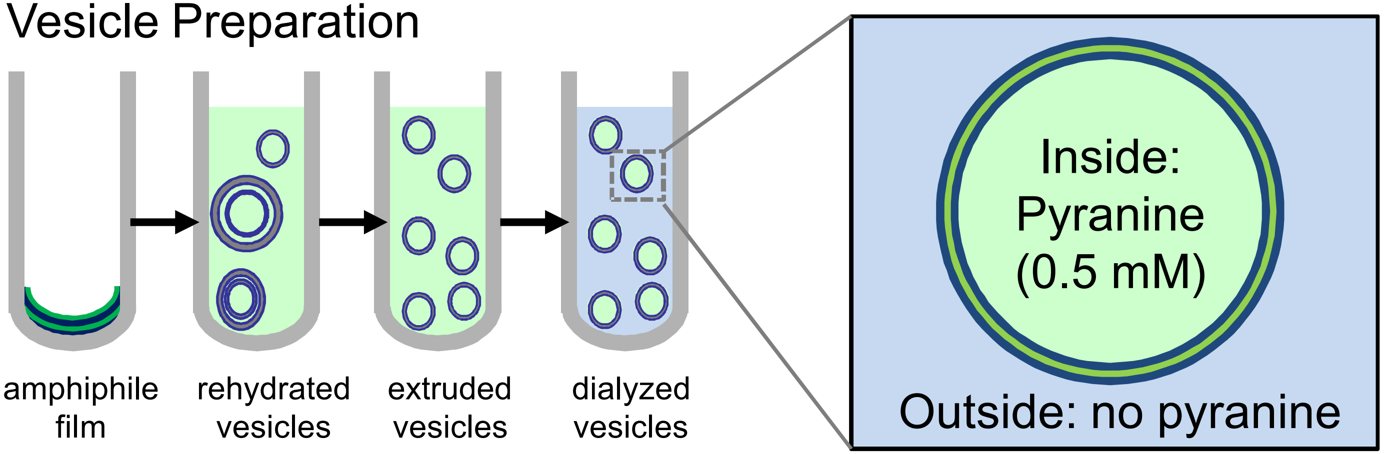


1. Permeability of OH^- is FAST → buildup of negative charge
2. Negative charge compensated by flux of the K^+ counterion…
3. …but permeability of K^+ is SLOW.
4. K^+ flux is the rate limiting step for net flux of OH^-

pH can be used to determine flux of K^+

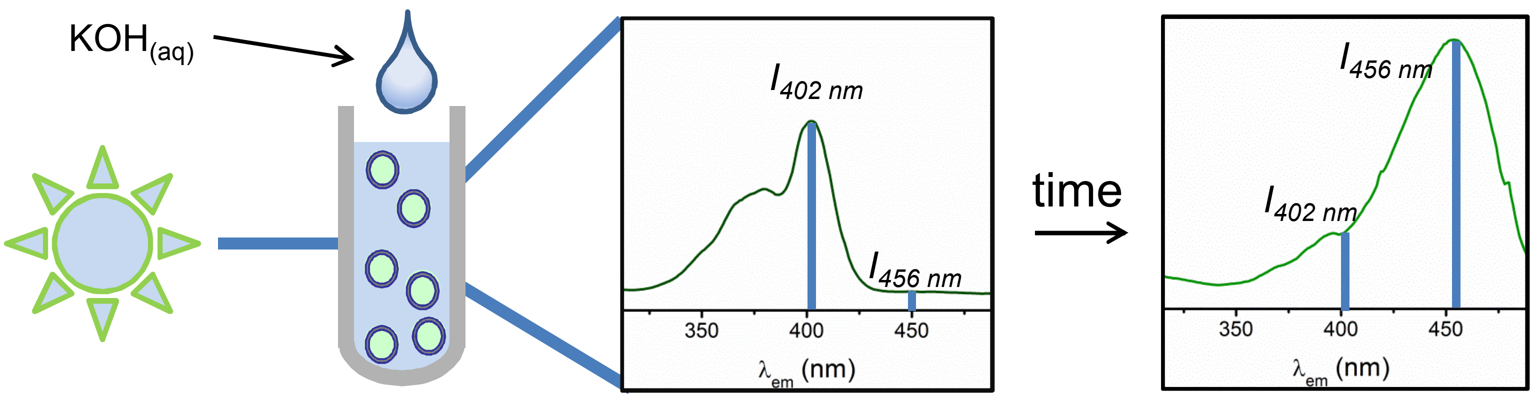
Ion Flux Monitored by Fluorescence

Vesicle Preparation



~200 nm vesicles ("unilamellar")

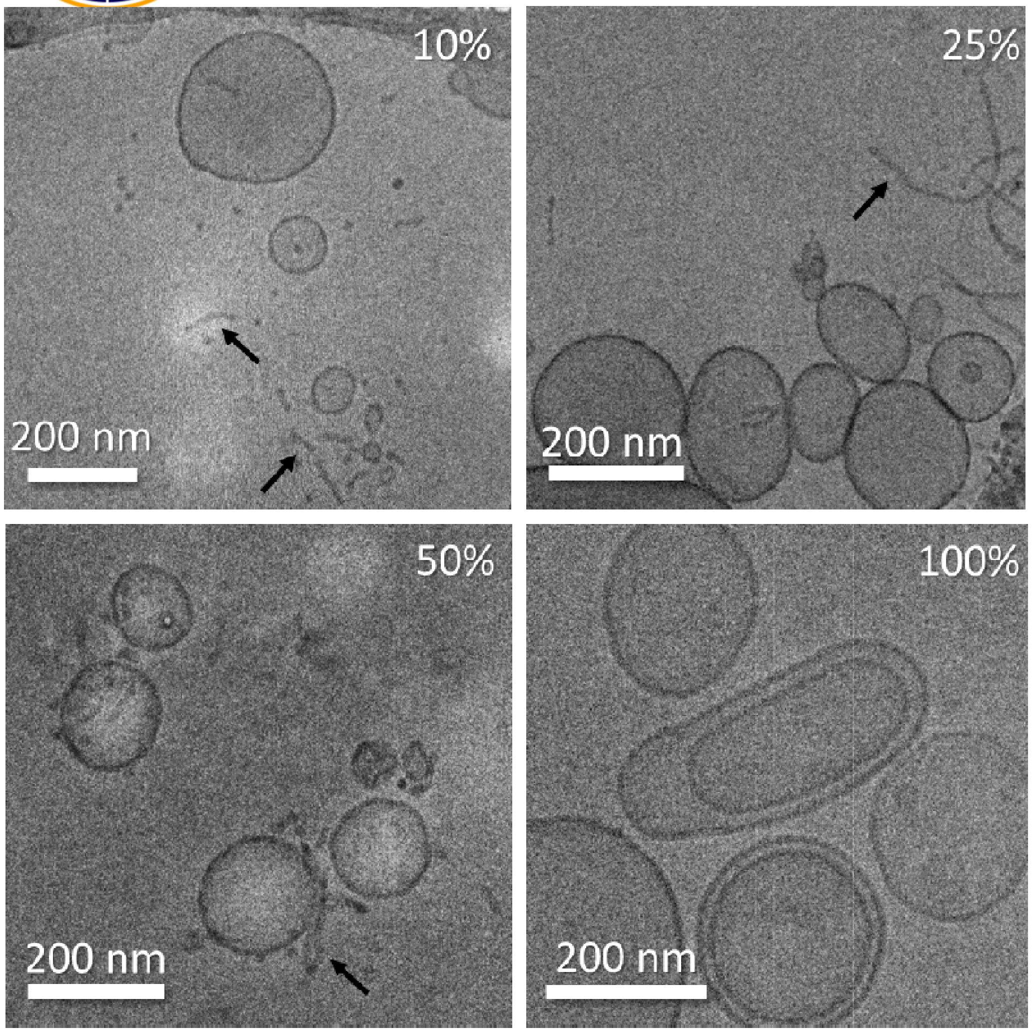
pH = 7 (PIPES/Sucrose)



$$\frac{I_{456\,nm}}{I_{402\,nm}} \rightarrow \mathrm{pH}_{t1}$$

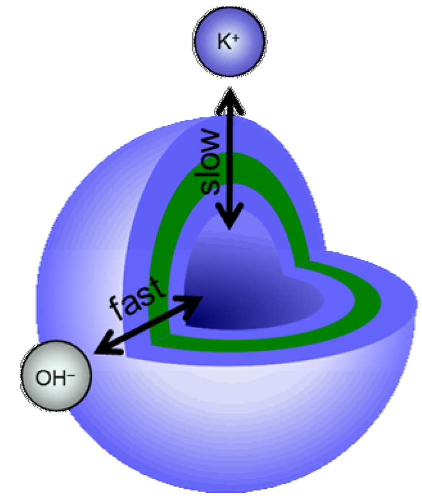
$$\frac{I_{456\,nm}}{I_{402\,nm}} \rightarrow \mathrm{pH}_{t2}$$

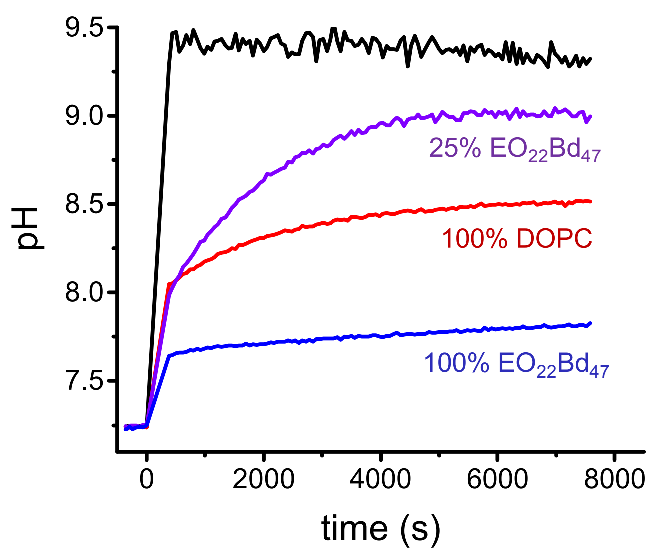
Ion Flux in Hybrid Vesicles



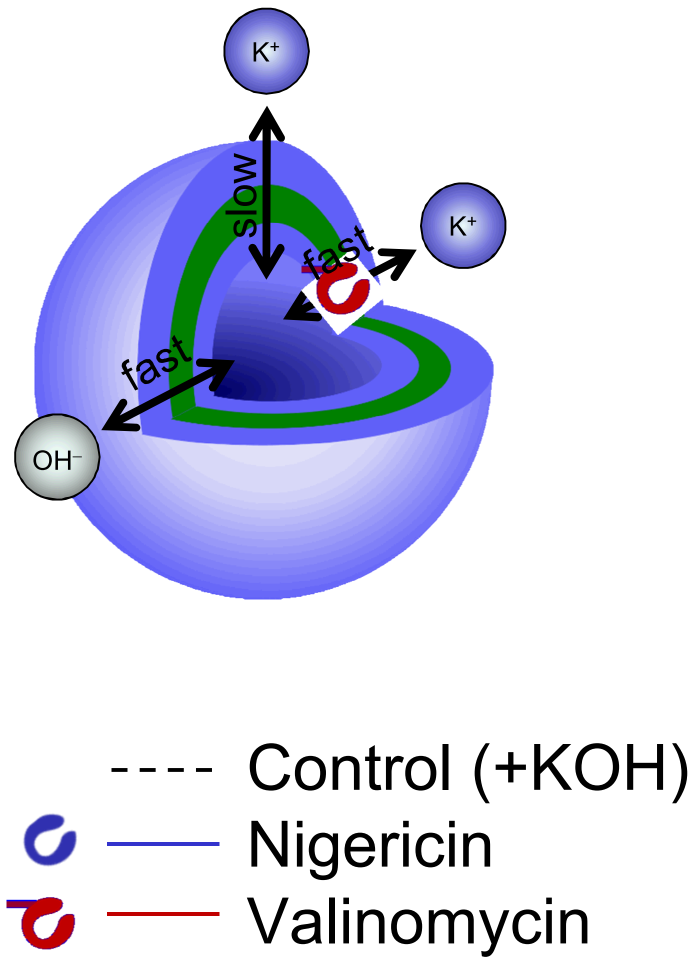
Good vesicles / Some worm-like micelles
Cryo-Em (Hae Ra Shin)

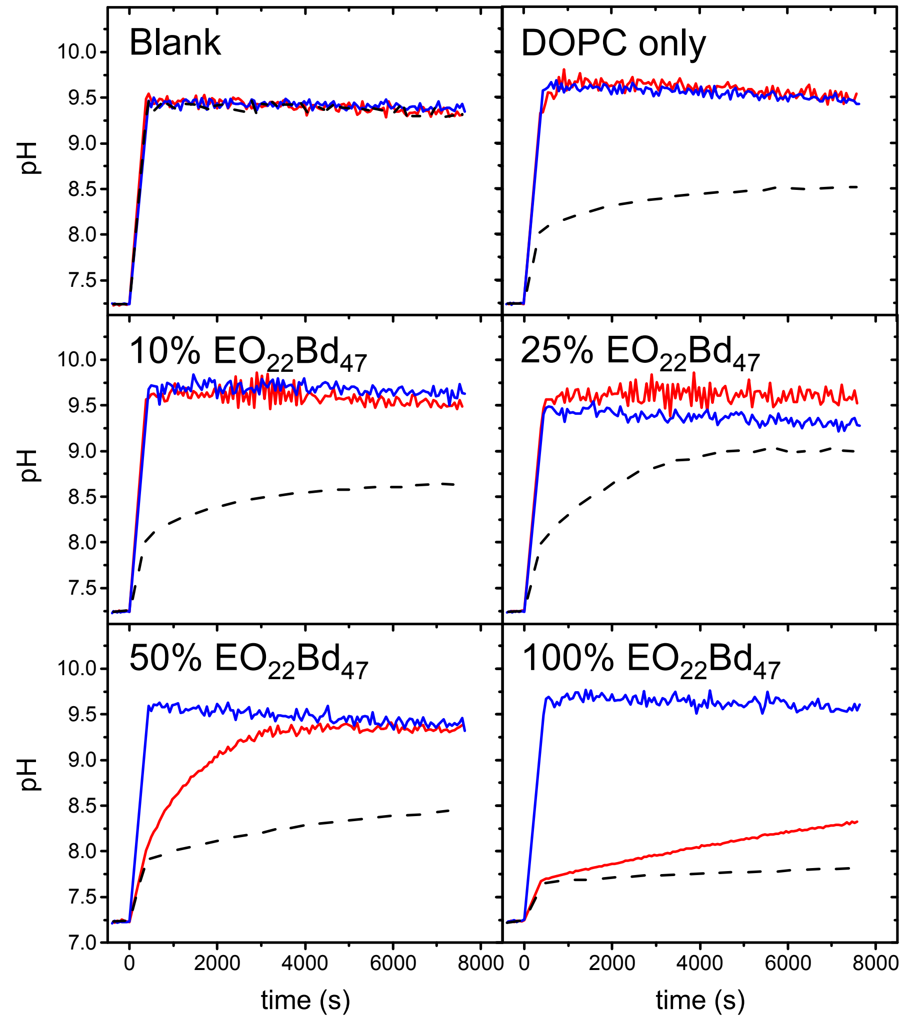
Hybrid Vesicle Permeability



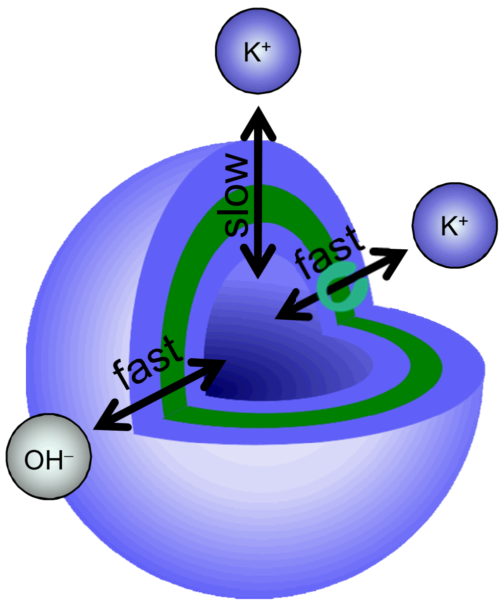


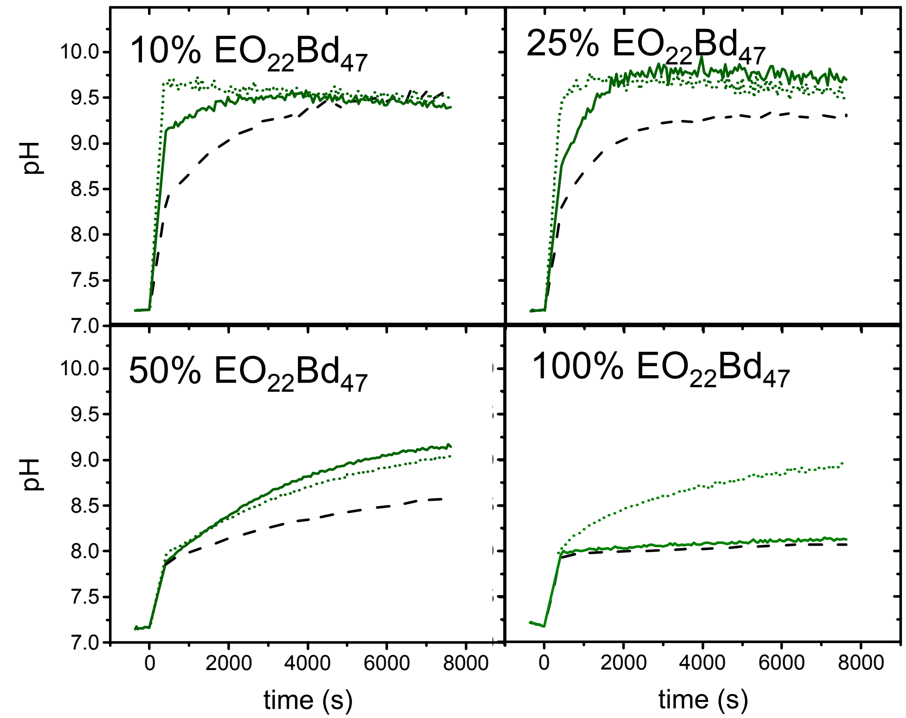
Modulating Permeability with Ionophores





Modulating Permeability with Ion Channels





---- Control (+KOH)

—— Gramicidin A (incubated <5 min)

········ Gramicidin A (rehydrated >5 days)

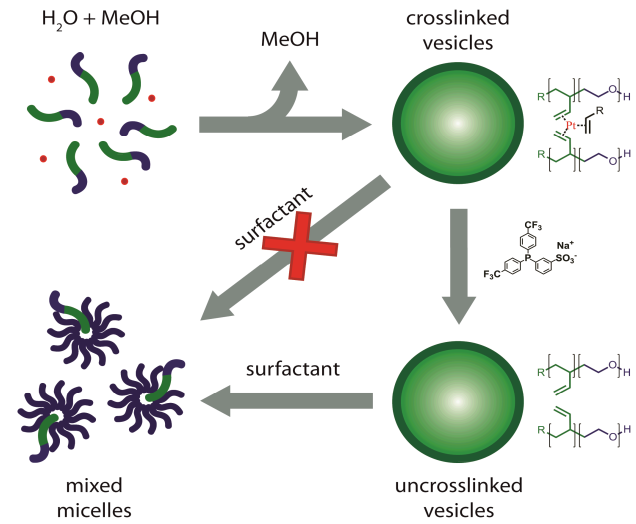
Summary and Conclusions

Used organometallic interactions to modulate the properties of "normal" polymersomes:

1. Enhanced Stability:
   - Pt--ǁ → Organometallic cross-links
   - Resistant to destabilization
   - Crosslinking can be selectively reversed w/ phosphine ligands

2. Catalytic Activity:
   - Pt centers still active
   - Enable hydrosilation reactions

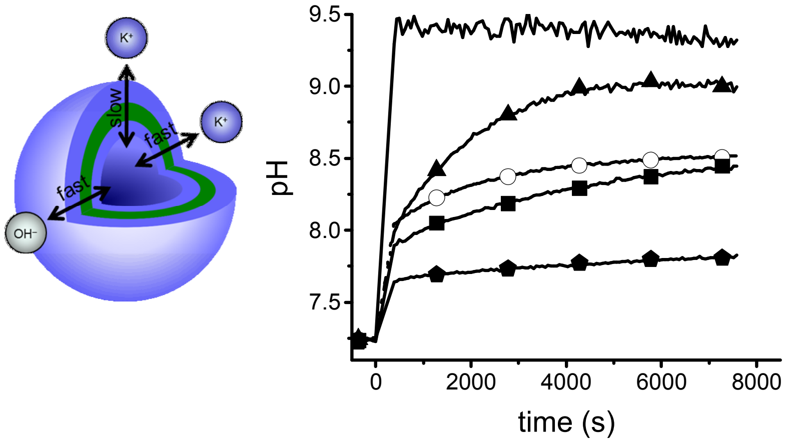
To produce soft self-assembling material that is both ***robust*** and ***dynamic***.



Monitoring and Modulating Ion Flux in Hybrid Bilayers

Key Accomplishments: Monitored and modulated ion flux in hybrid vesicles via reconstituted membrane proteins. Prepared and characterized hybrid polymer/lipid bilayers and assessed their fluidity.

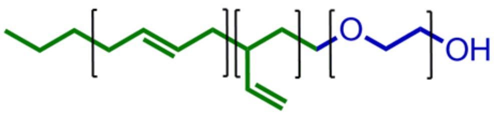
IMPACT: The permeability and lateral fluidity of hybrid bilayers is important to our research and has not been explored in the literature. Our work produced a manuscript of general interest currently under review, and another in preparation.



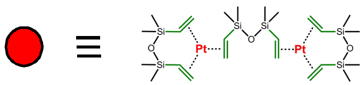
Team and Acknowledgments

Dr. Walter Paxton (CINT Staff)
Dr. Ian Henderson (Omphalos)
Hope Quintana (NMSU/LANL)
Dr. Julio Martinez (NMSU)
Patrick McAninch (CINT intern)
Dr. Hae Ra Shin (CINT postdoc)
Dr. Komandoor Achyuthan (Sandia)
Dr. George Bachand (CINT Staff)
Prof. Aaron Collins (SNHU)
Dr. Nathan Bouxsein (Perspectives)
Dr. Sergei Ivanov (CINT Staff)
Dr. Gabriel Montano (CINT Staff)

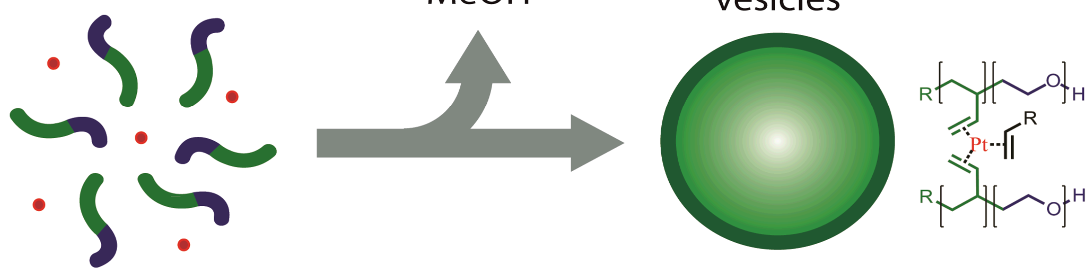
Forming Cross-linked Vesicles with Pt and PEO-PBd



$EO_{21} - Bd_{32}$ (1,2 addition)



Karstedt's catalyst



Karstedt's / PEO-PBd in MeOH

↓

Add H_2O / Remove MeOH

↓

60-100 nm vesicles