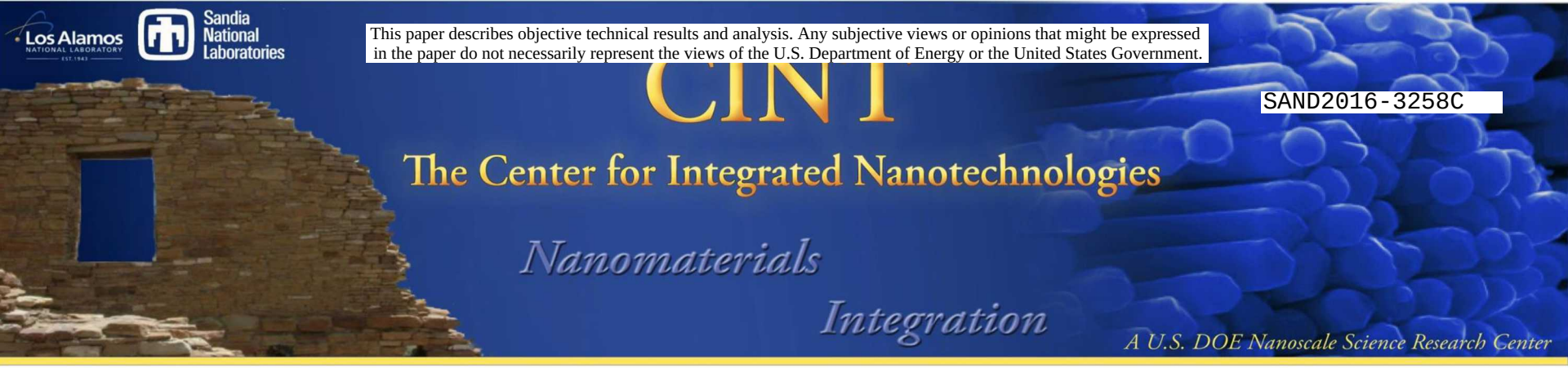
SAND2016-3258C




# Capable Cross-Links: Polymersomes Reinforced with Catalytically Active Metal–Ligand Bonds

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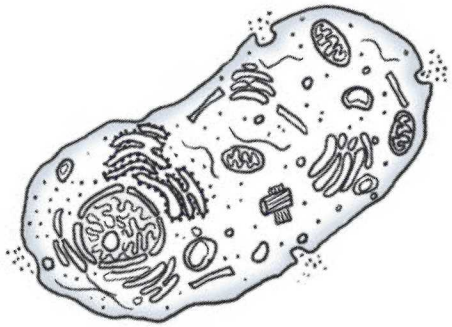
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

# Mimicking Biological Membranes

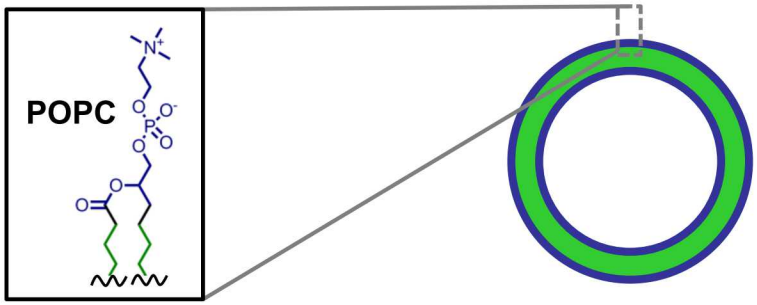
**Properties**
- Radial/Axial Asymmetry
- Chemical Diversity
- Functional Components

**Functions**
- Mass transport
- Energy transduction
- Information flow
- Protection



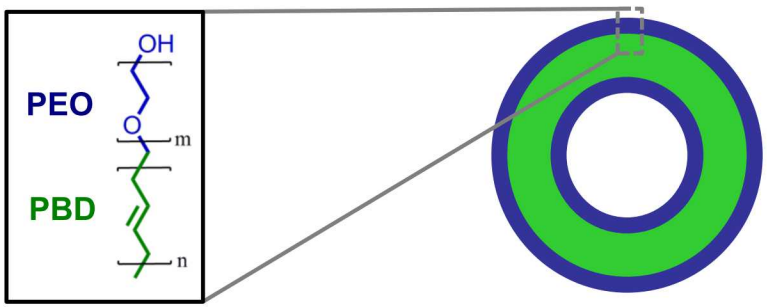
How can we incorporate or mimic **properties** and **functions** of biological cells to create robust **advanced materials**?

## Liposomes



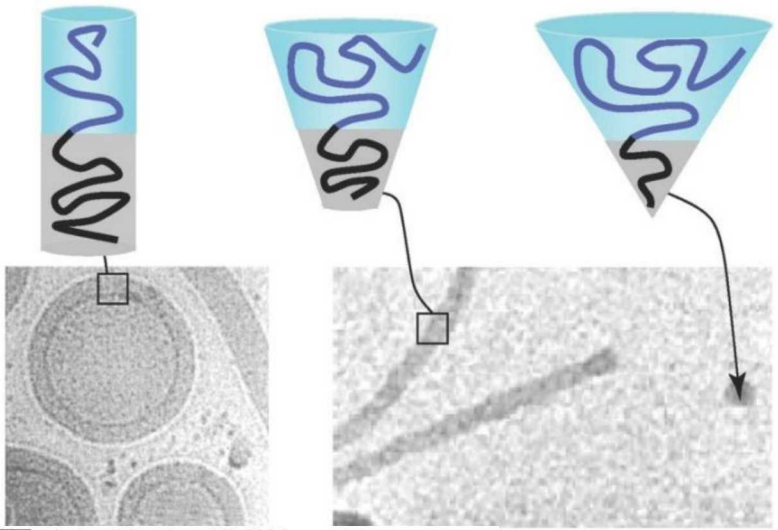

**2 Major Challenges:**
Limited Chemical and Mechanical Stability
Limited Modification Chemistries

## Polymersomes

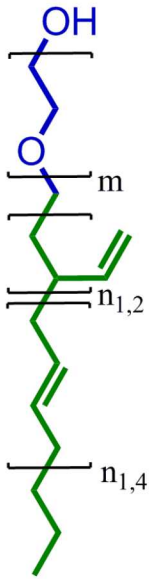



**Polymersomes Can Help**
*Enhanced* Chemical and Mechanical Stability
*Unlimited* Modification Chemistries

# PEO-PBd Polymer Vesicles



Dischер DE, Ahmed F. 2006.
Annu. Rev. Biomed. Eng. 8:323–41

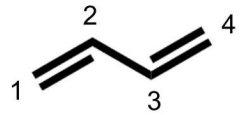



ring opening

1,2 addition

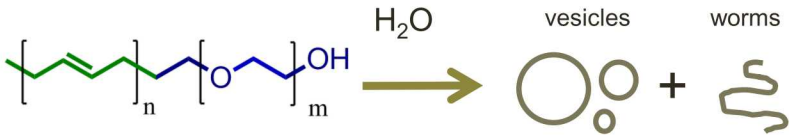
1,4 addition

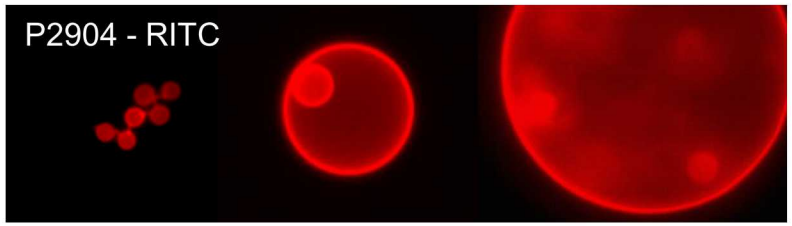

ethylene oxide

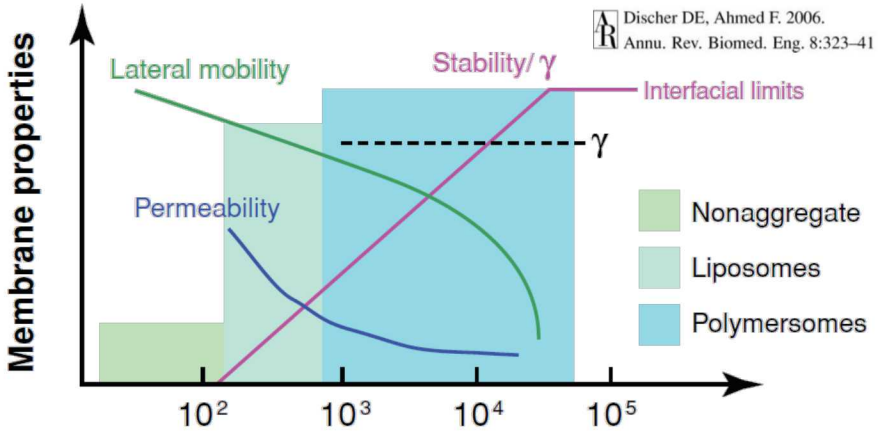



butadiene

*Polymer Source Inc.*

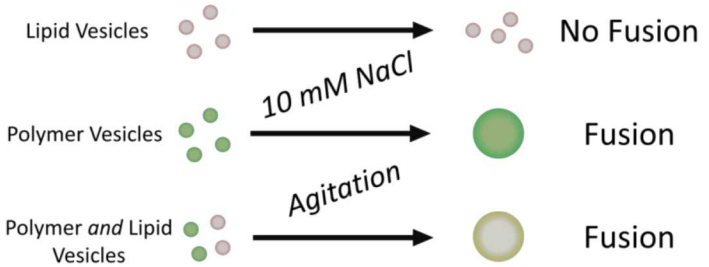



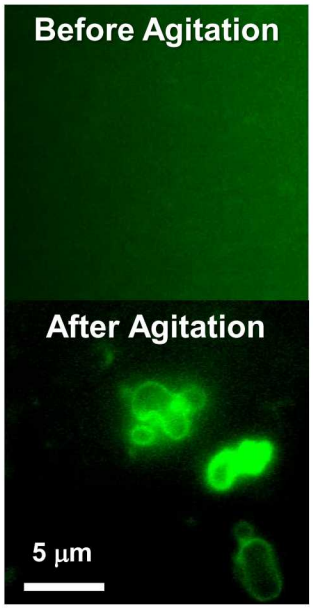




Dischер DE, Ahmed F. 2006.
Annu. Rev. Biomed. Eng. 8:323–41

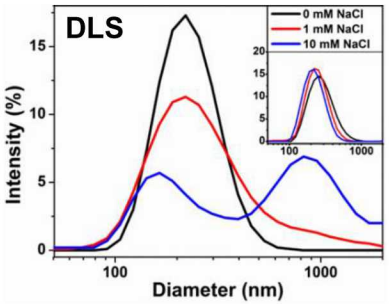
# *Dynamic* Polymer Vesicle Membranes

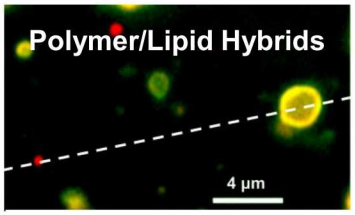
## Mechanically-Activated Fusion



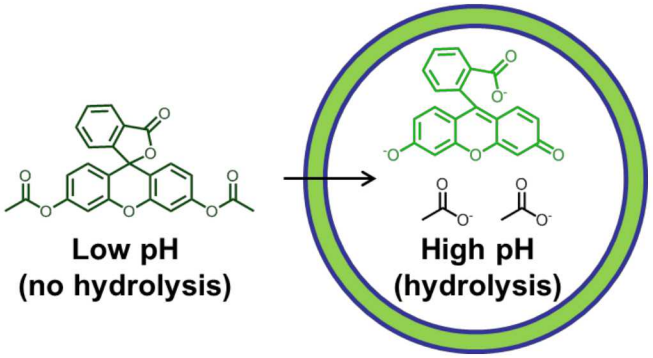

**Vesicle Sizes After Agitation**



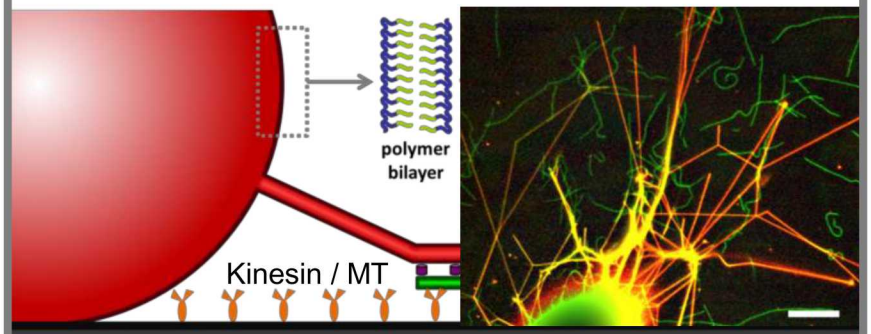

I. M. Henderson, W. F. Paxton, *Angew. Chem. – Int. Ed.* ***2014,*** *53,* 3372-3376; *J. Poly. Sci. B,* **2014,** *53,* 297–303

## Lysosome-Mimicking Vesicles



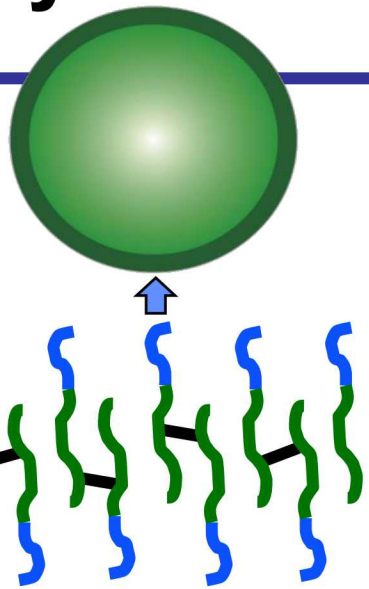

W. F. Paxton et al. *Soft Matter* **2013,** *9,* 11295–11302

## Dynamic Assembly of Polymer Nanotubes

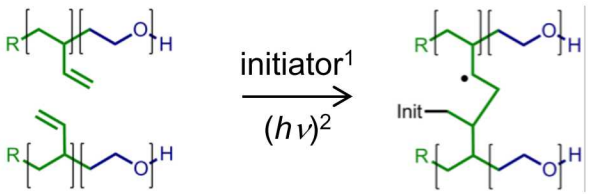



W. F. Paxton et al. *Nanoscale,* **2015,** *7,* 10998–11004

# *ROBUST* Polymer Vesicles Membranes

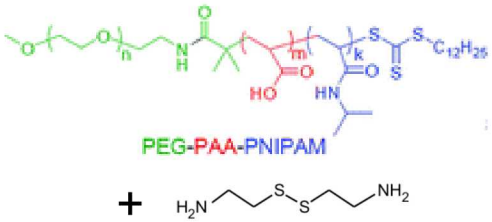


## Radical cross-linking



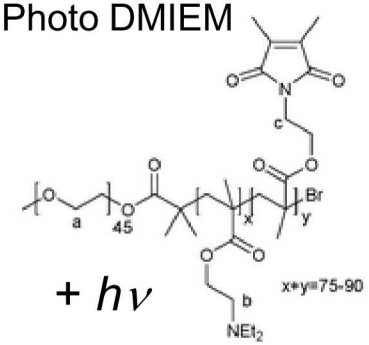

1. Discher et al. *JPCB* **2002,** *106,* 2848.
2. Jofre et al. *JPCB* **2007,** *111,* 5162.

## Amide coupling…



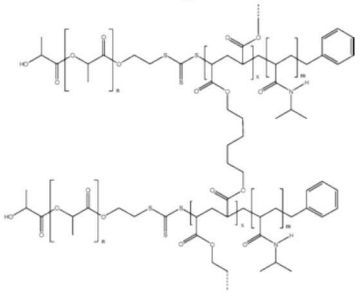

Zhiyuan Zhong et al. *J. Mater. Chem.*, **2011,** *21,* 19013.

## Photo DMIEM



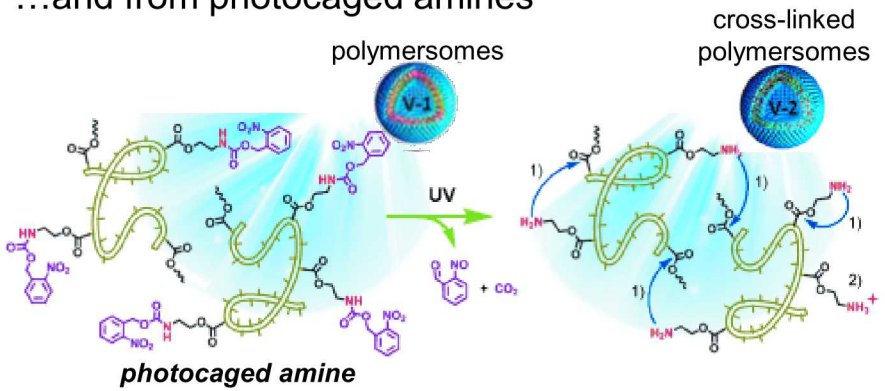

Voit et al. *Chem. Commun.* **2011,** *47,* 3466-3468.

## RAFT + diacrylate



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

## …and from photocaged amines

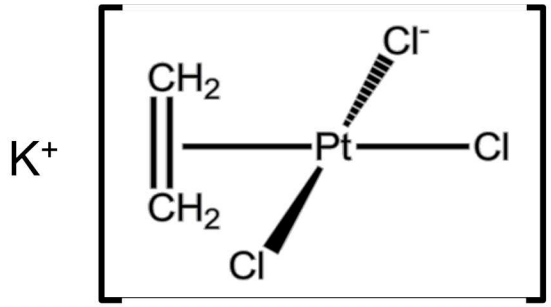



Shiyong Liu et al. *Angew. Chem.* **2014,** *53,* 3138.

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

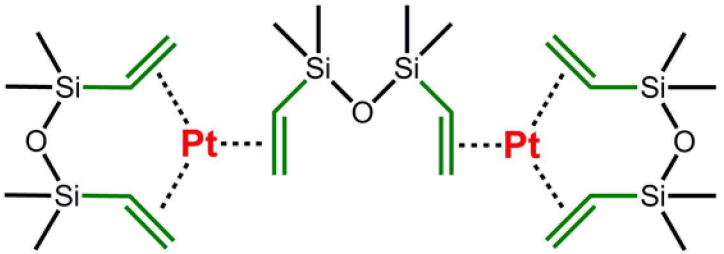
# Platinum-Alkene Complexes

## Zeise's Salt



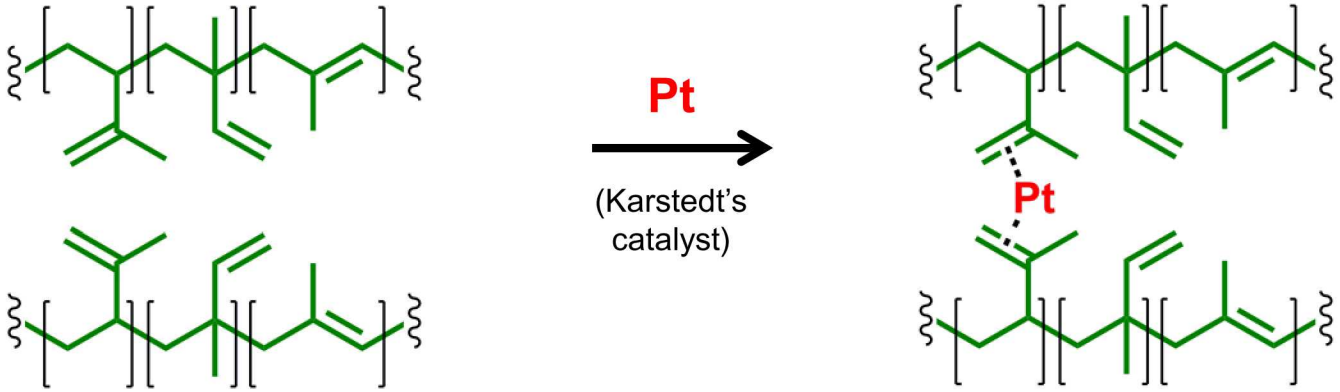

$\eta^2$-alkene compound (1831)

## Karstedt's Catalyst

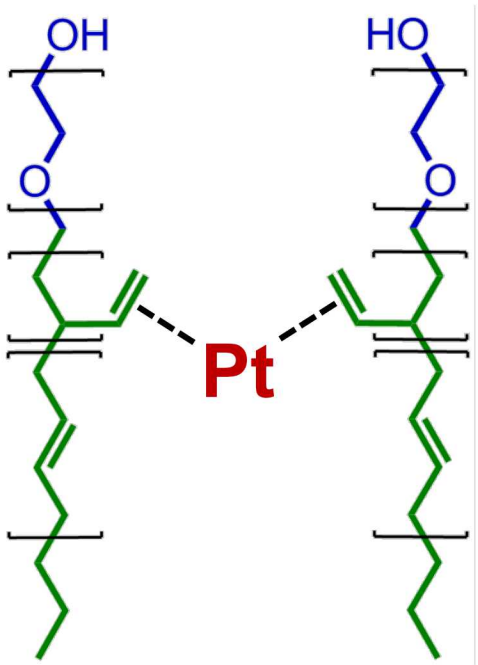



$\eta^2$-alkene compound (1973)
hydrosilylation catalyst

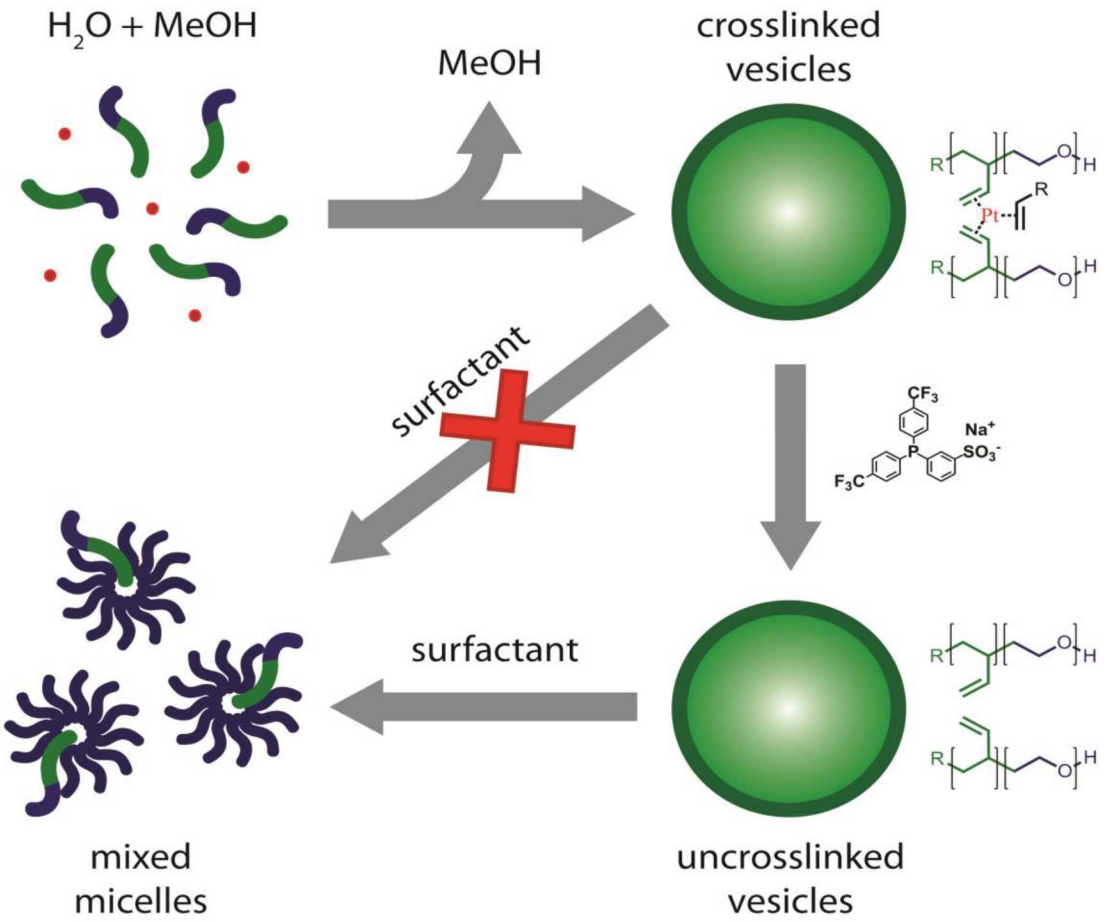
## Isoprene–Pt(0) Coordination (Rupar et al. *JACS*, **2011**)



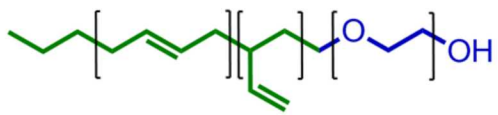
# Capable Crosslinks: Polymersomes Reinforced with Catalytically Active Metal-Ligand Bonds



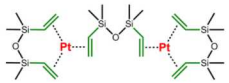

Exploit organometallic interactions to create membranes that are both ***robust*** and ***dynamic***.



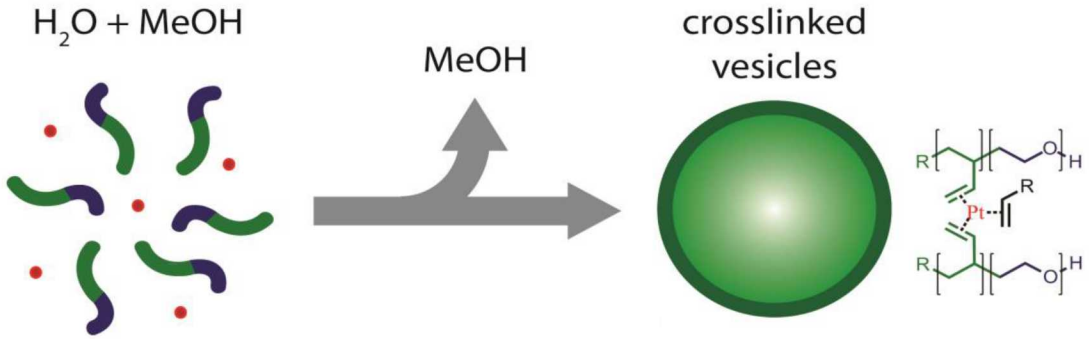
# Forming Cross-linked Vesicles with Pt and PEO-PBd




$EO_{21} – Bd_{32}$ (1,2 addition)

● ≡ 

Karstedt's catalyst



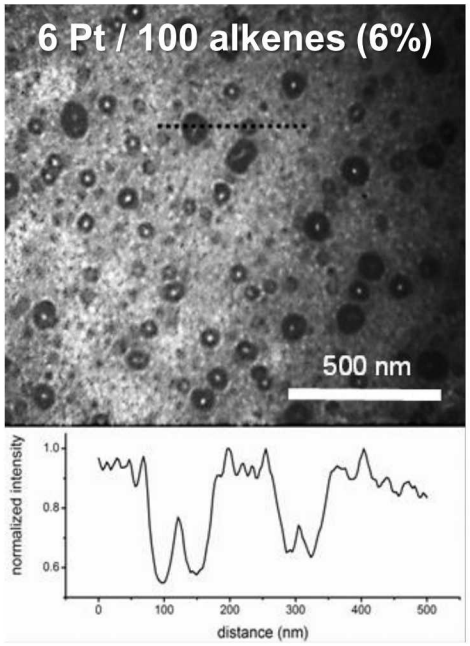

Karstedt's / PEO-PBd in MeOH

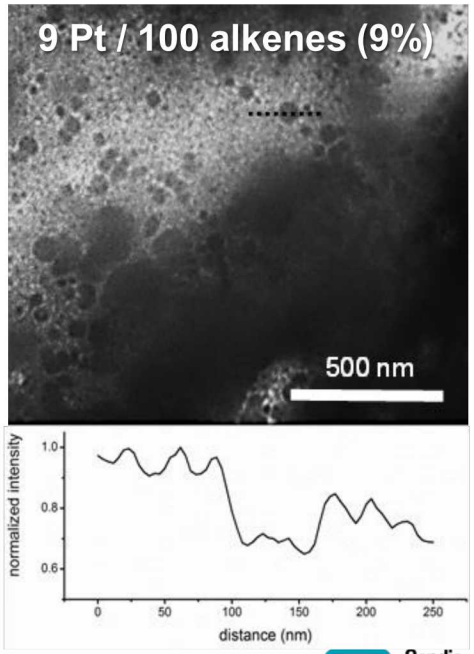
↓

Add $H_2O$ / Remove MeOH

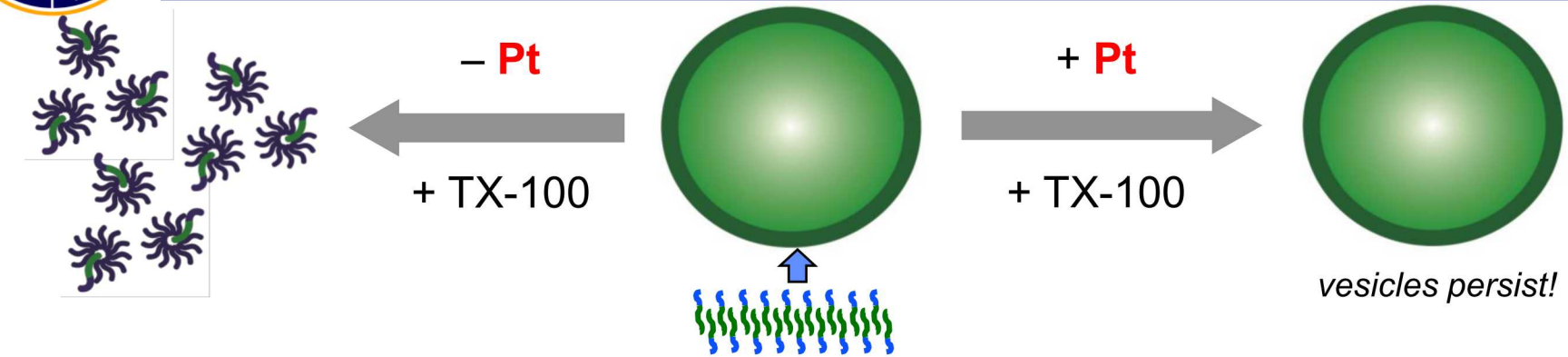
↓

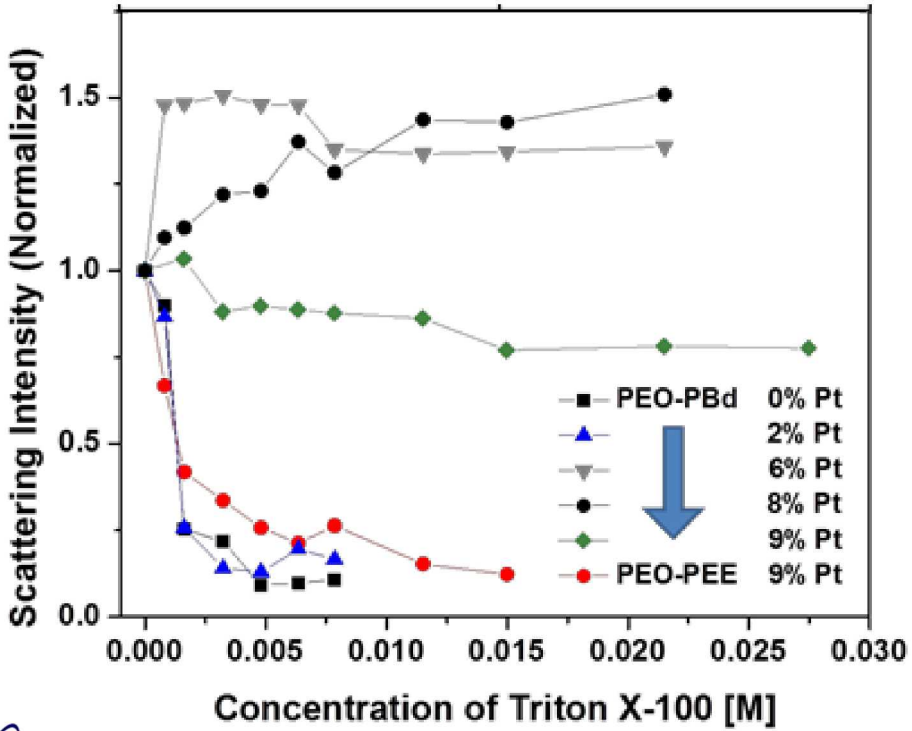
***60-100 nm vesicles***

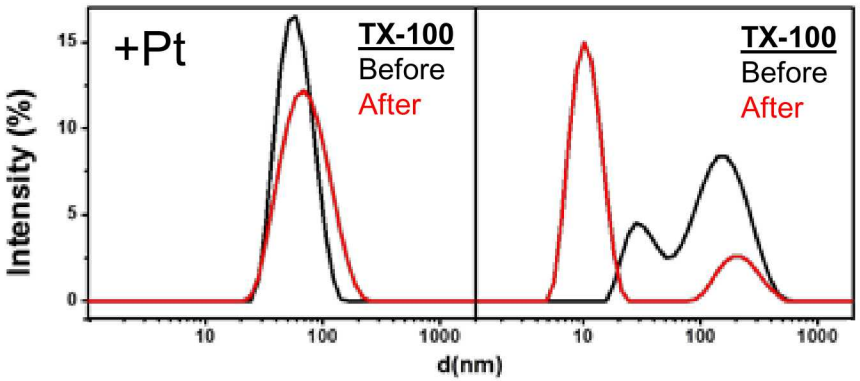


# Surfactant-Resistant Cross-linked Polymersomes



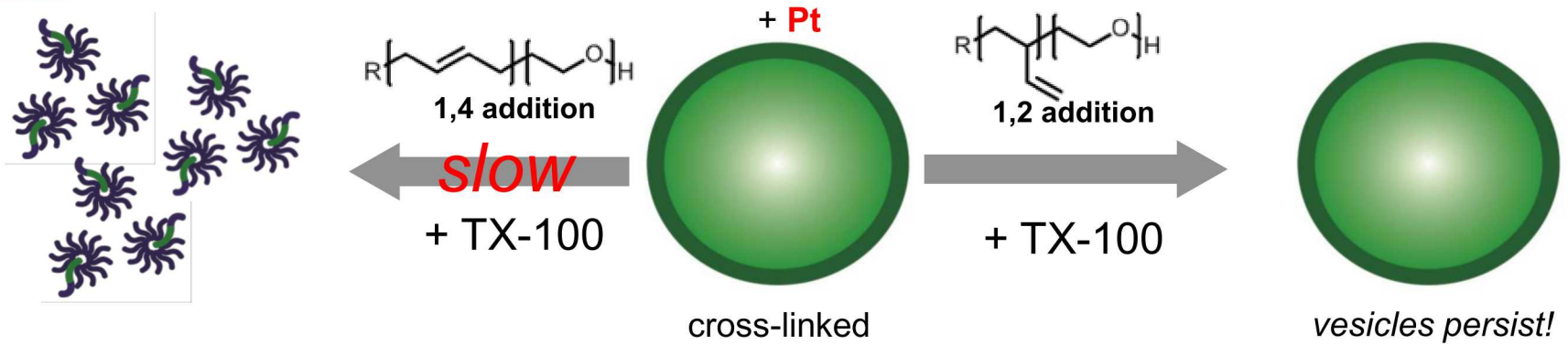



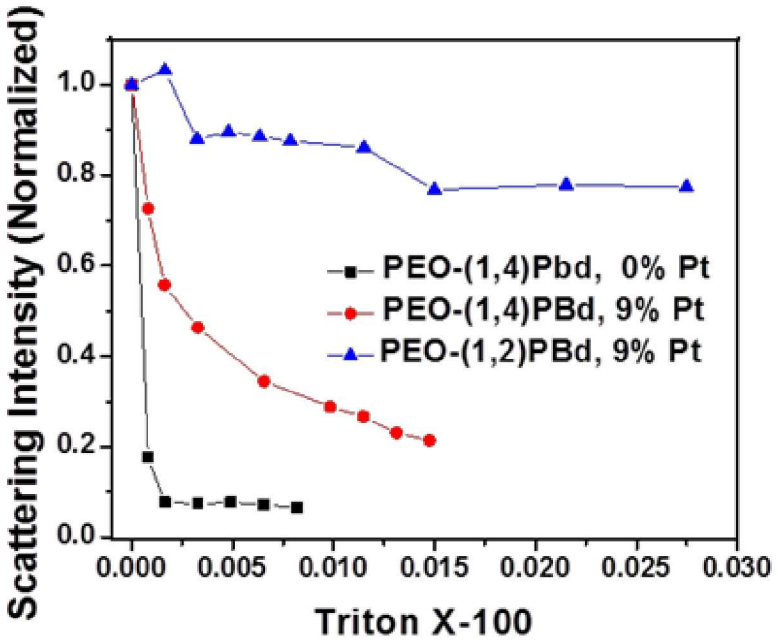




Uncross-linked vesicles → mixed micelles

***Cross-linked vesicles resist surfactant***

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



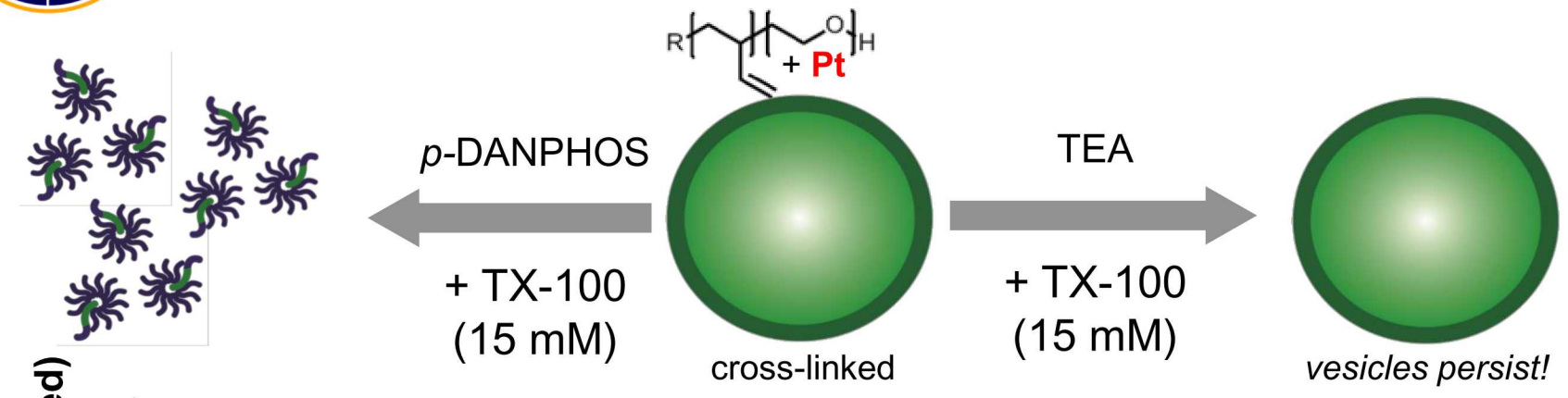

1,4 PBd is *MORE* resistant with **Pt**…

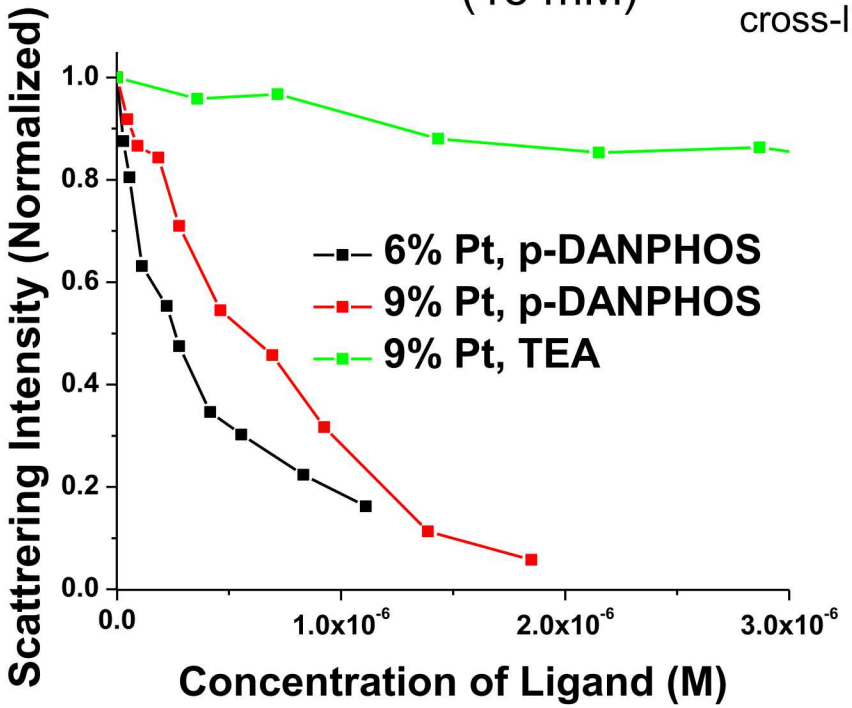
…but *LESS* resistant than 1,2 PBd

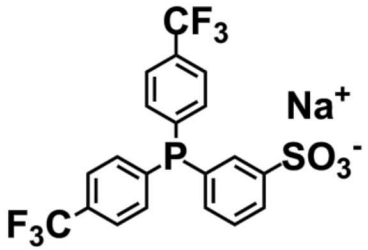
**Two effects:**

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

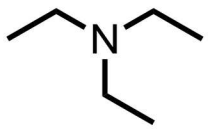
# Selective Reversibility w/ a Competing Ligand



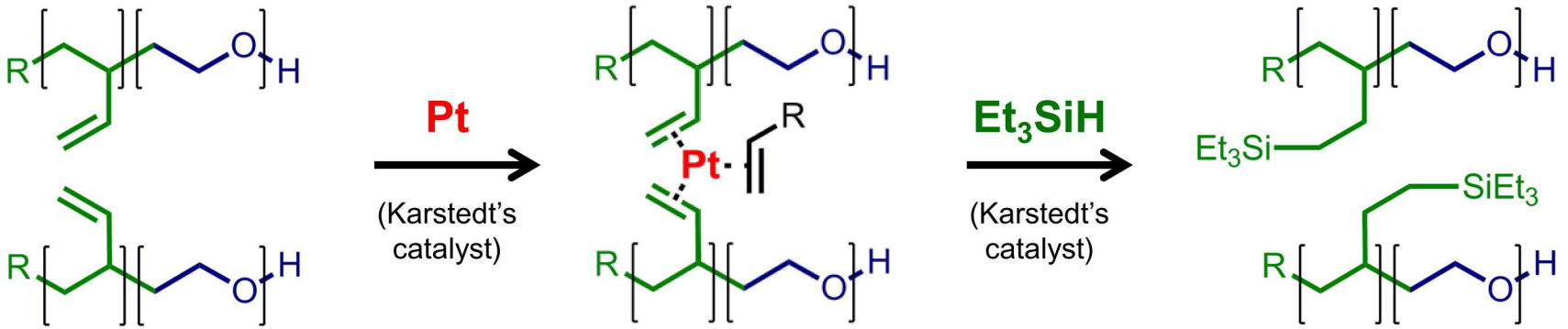

*p*-DANPHOS
bis(4-trifluoromethylphenyl)(3-sulfonatophenyl)phosphine

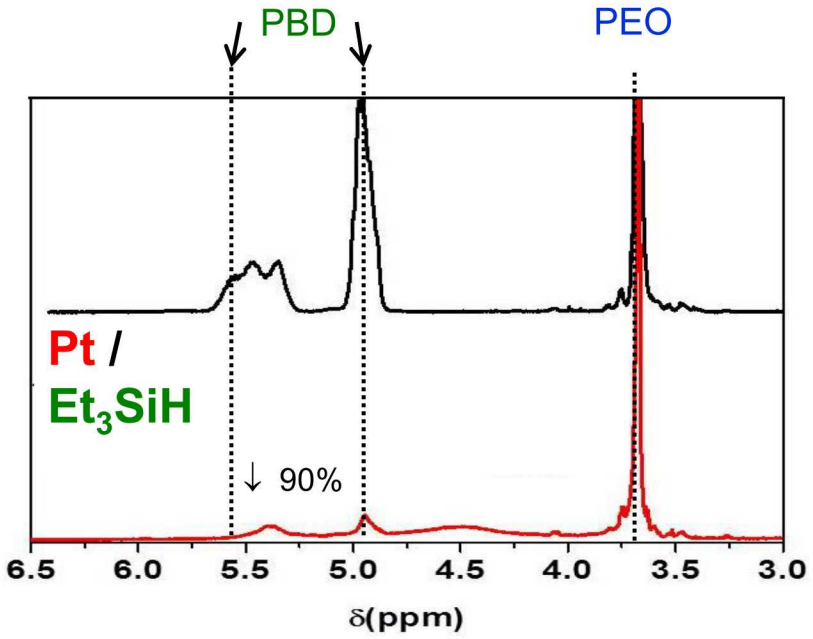



TEA
triethylamine

***Reversible/Dynamic Cross-links via Competitive ligands***

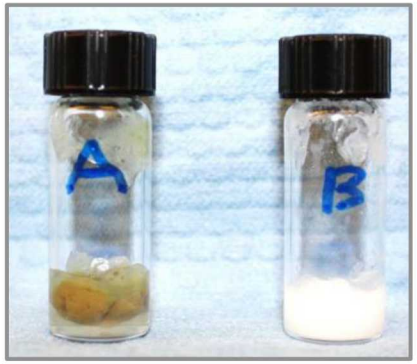
# Pt in Cross-linked Polymersomes Are Catalytically Active




**1 h Agitation:**

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




***Catalytically-Active Cross-links***

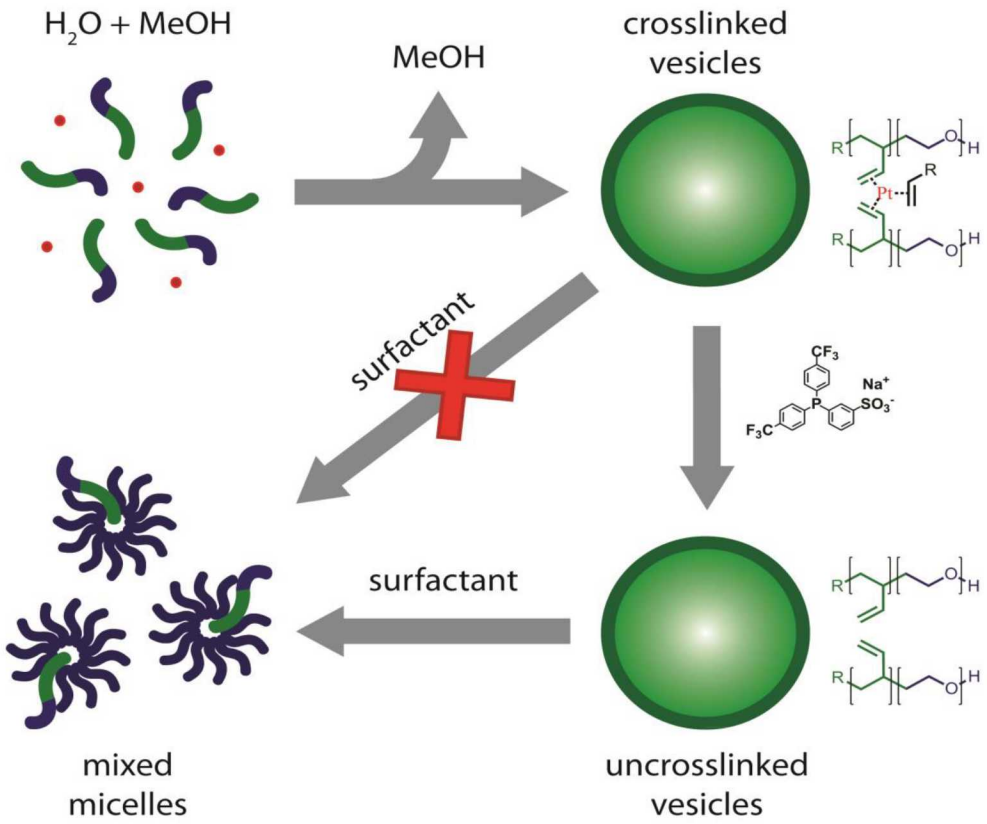
# Conclusions

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

1. Enhanced Stability:
   - Pt--‖ → 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***.



# Acknowledgements

Ian Henderson
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(NMSU/LANL)

Julio Martinez
(NMSU)

Sergei Ivanov
(CINT)

## Center for Integrated Nanotechnologies

*Helping you understand, create, and characterize nanomaterials*

The DOE/SC nanoscience centers:

- Are defined by a scientific field, not specific instrumentation.
- NSRC staff support user projects and conduct original research.
- Capabilities involve expertise, hardware and software.
- Users access Synthesis, Fabrication, Characterization and Theory capabilities.