

**Green Chemistry:  
Inventing a Circular Economy**

**John C. Warner**

President and CTO  
warnerbabcock institute for green chemistry  
john.warner@warnerbabcock.com

Co-founder  
beyondbenign green chemistry education  
john@beyondbenign.org

@johnwarnerorg





**Polaroid**

warnerbabcock  
institute for green chemistry

AAAS-LEMELSON  
Invention Ambassadors

MassDEP  
California Department of  
Toxic Substances Control

UNITED STATES  
ENVIRONMENTAL PROTECTION  
AGENCY

REACH  
COMPLIANCE

GSSP  
solving of complex, multi-  
problem

beyondbenign  
green chemistry education



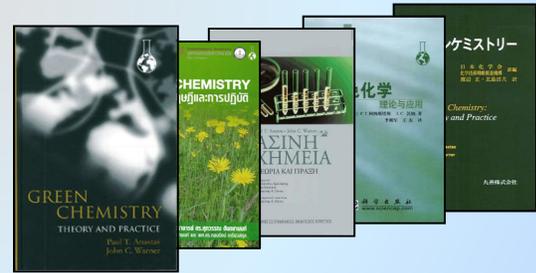








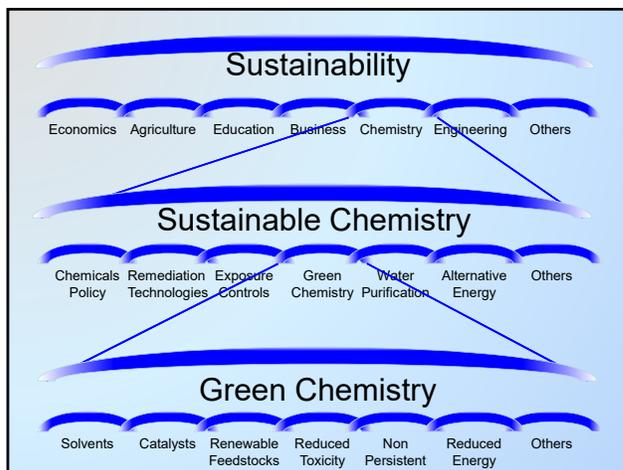
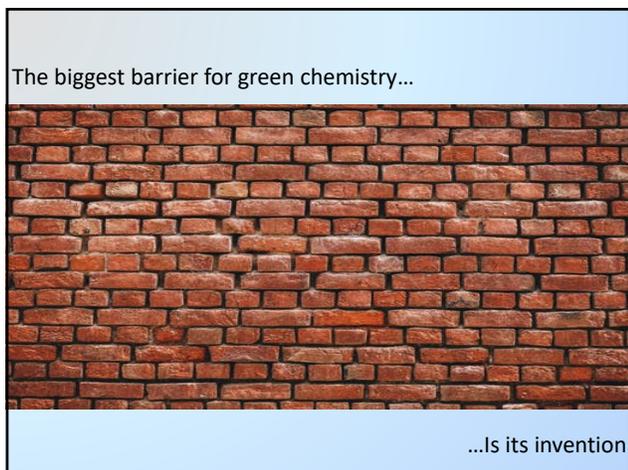
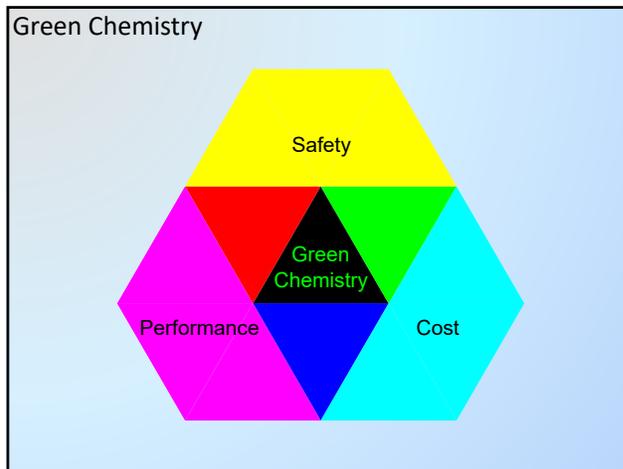
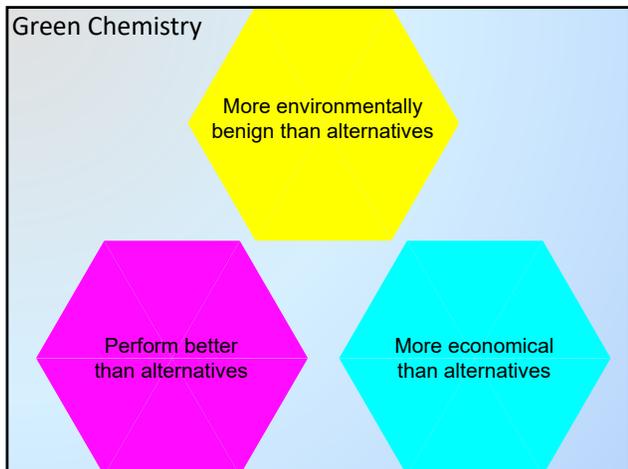


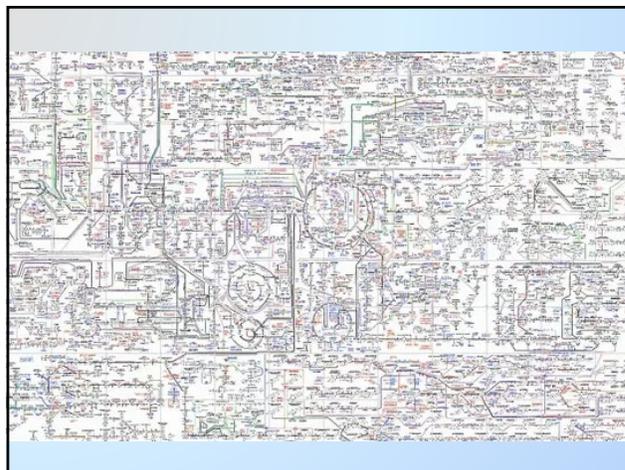
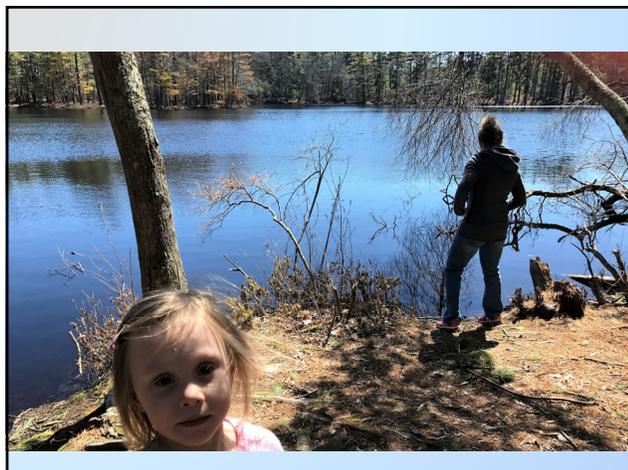
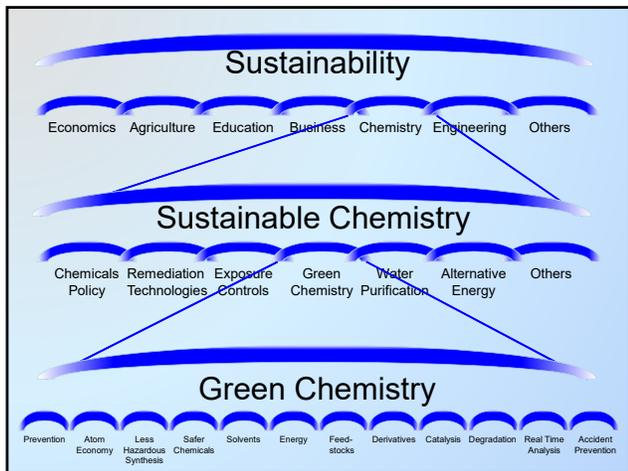


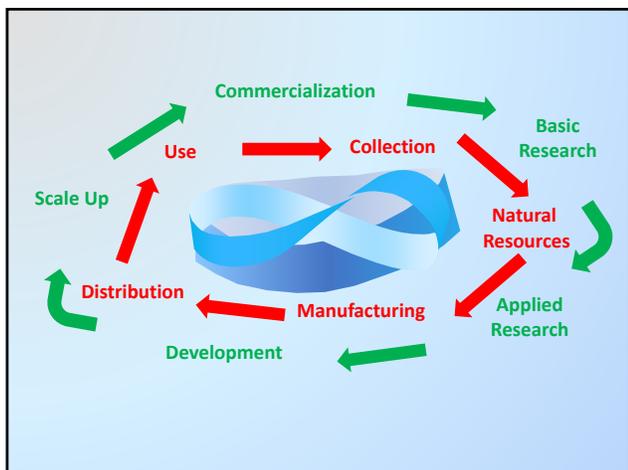
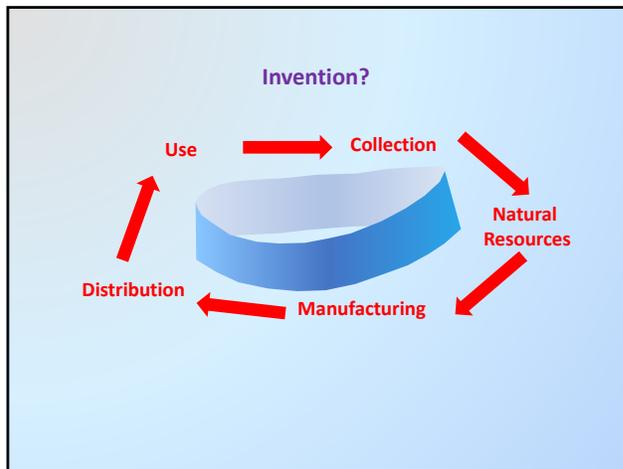
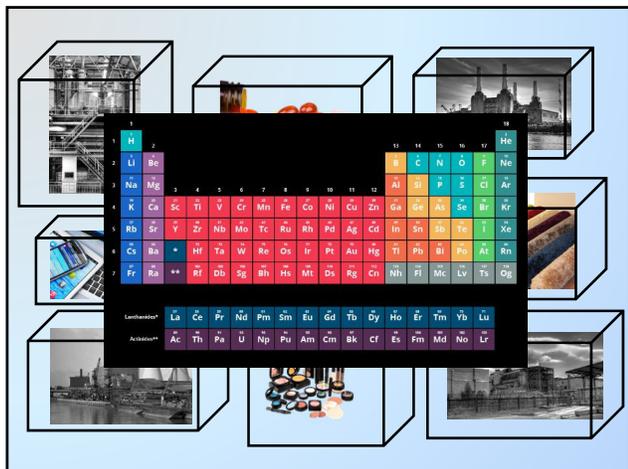
**Green Chemistry**  
is the *design* of chemical products and  
processes that reduce or eliminate the *use*  
*and/or generation* of hazardous substances.

### The Twelve Principles of Green Chemistry

1. **Prevention.** It is better to prevent waste than to treat or clean up waste after it is formed.
2. **Atom Economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Synthesis.** Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Designing Safer Chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
5. **Safer Solvents and Auxiliaries.** The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
6. **Design for Energy Efficiency.** Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of Renewable Feedstocks.** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.
8. **Reduce Derivatives.** Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. **Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for Degradation.** Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.
11. **Real-time Analysis for Pollution Prevention.** Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.
12. **Inherently Safer Chemistry for Accident Prevention.** Substance and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.







**Enthalpy and Entropy**

"The greatest mind in American History"  
- Albert Einstein



Josiah Willard Gibbs  
February 11, 1839 - April 28, 1903

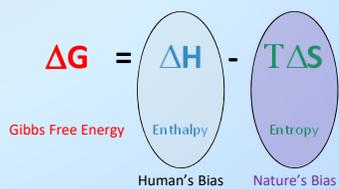
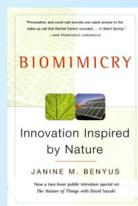
$$\Delta G = \Delta H - T\Delta S$$

Gibbs Free Energy    Enthalpy    Entropy

## Molecular Biomimicry



Janine Benyus



## Molecular Mechanisms of Sustainable/Circular Materials

1. Equilibrium Discontinuities
2. Collaborative Structures
3. Pre-associative Reactivity
4. Synchronous Orthogonal Mechanisms
5. Resilience and Molecular Diversity

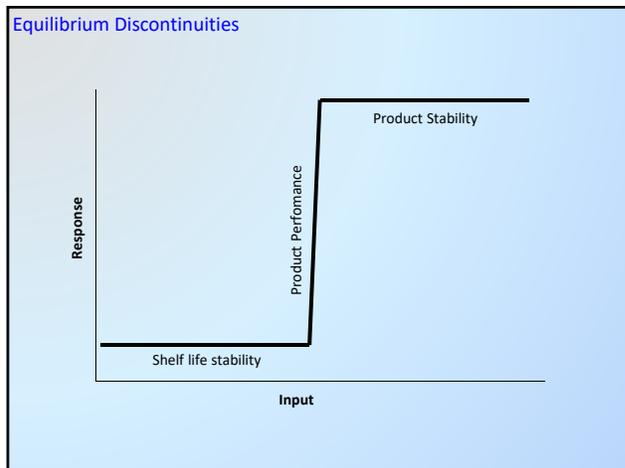
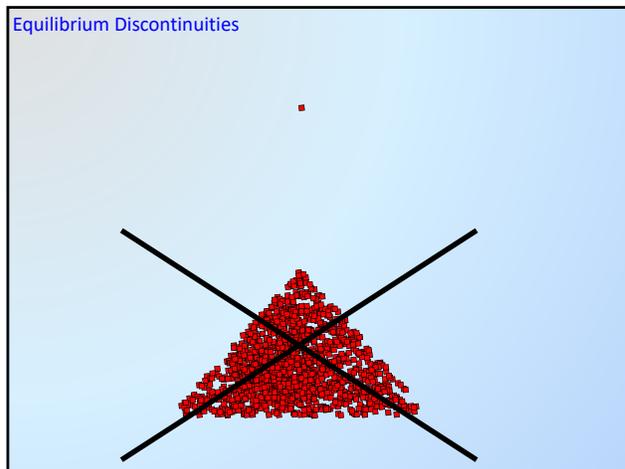
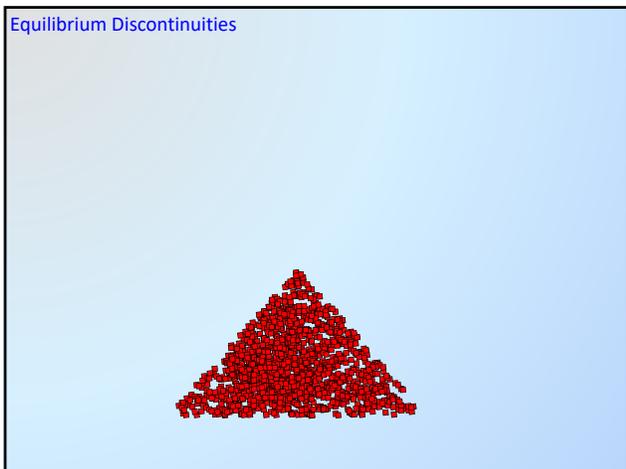
## Molecular Mechanisms of Sustainable/Circular Materials

1. **Equilibrium Discontinuities**
2. Collaborative Structures
3. Pre-associative Reactivity
4. Synchronous Orthogonal Mechanisms
5. Resilience and Molecular Diversity

## Equilibrium Discontinuities


 Rene Thom  
 September 2, 1923 – October 25, 2002


Catastrophe Theory



### Construction Materials: Asphalt Paving

Monday, November 25, 2013

17°F (-8°C)  
70% Recycled Material

Novel asphalt binder additive compositions and methods of use. Warner, John C.; Muollo, Laura Rose; Walker, Rowan Lewis; Bianchini, Jason R., Priority Date: November 11, 2013, US 2018/0257985.  
Asphalt binder additive compositions and related methods. Warner, John C.; Muollo, Laura Rose; Walker, Rowan Lewis; Bianchini, Jason R., Priority Date: November 11, 2013, US 9,954,485, WO 2014/070180, EP 3107958, JP 2015237487.

**COLLABORATIVE**  
ASPHALT ADDITIVES LLC

**Delta-S**

### Hair and Fabric Shaping and Toning

\*Photoreactive Polymers and Devices for use in Hair Treatments\* Warner, John C.; Cannon, Amy S.; Raudys, Jennifer; Undurs, Arundhati; PCT Int. Appl. WO 2004058187. Filed December 22, 2003. Published December 23, 2004. CA 2510362. Filed December 22, 2003. Published July 15, 2004. EP 1575537. Filed December 22, 2003. Published September 21, 2005.  
\*Photoinduced Copolymer Functionalized Substrates\* Warner, John C.; Cannon, Amy S.; Dye, Kevin PCT Int. Appl. WO 2007139810. Filed May 23, 2007. Published December 6, 2007.

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### Collaborative Structures

Take workshops!  
Get better at what you don't do well!

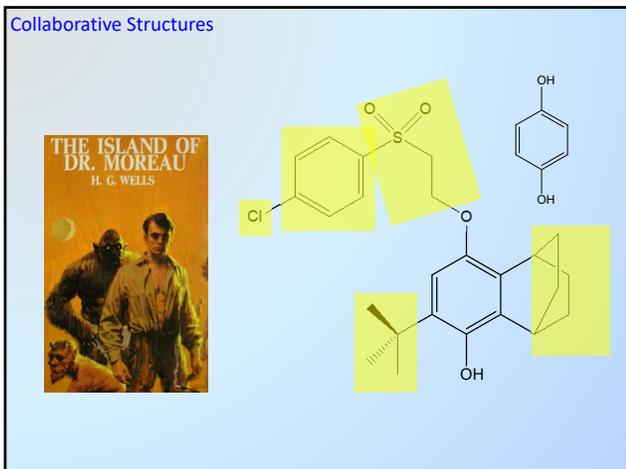
I am good at math!

I am good at communication!

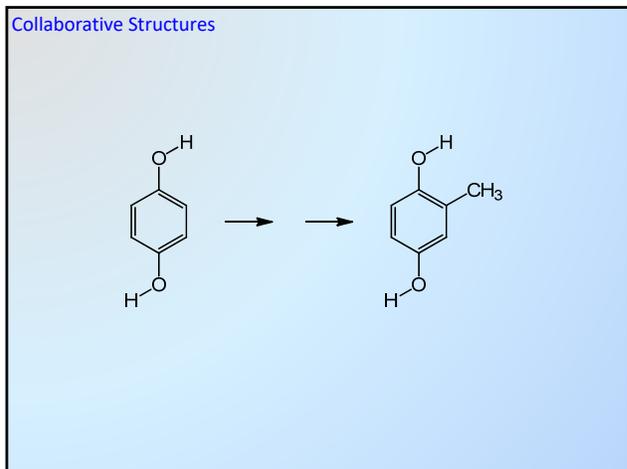
Collaborate!

Do more of what you love to do!

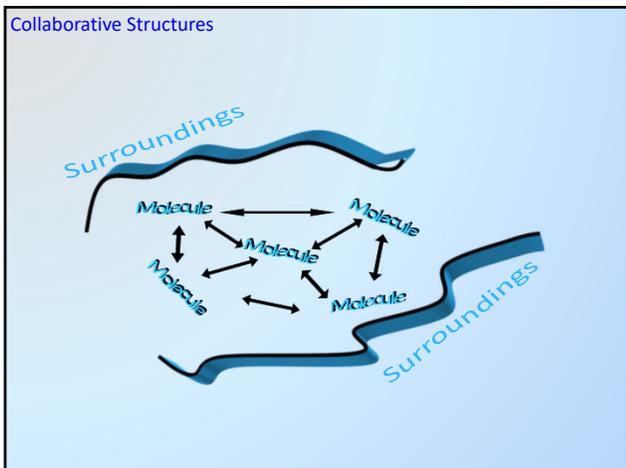
Collaborative Structures



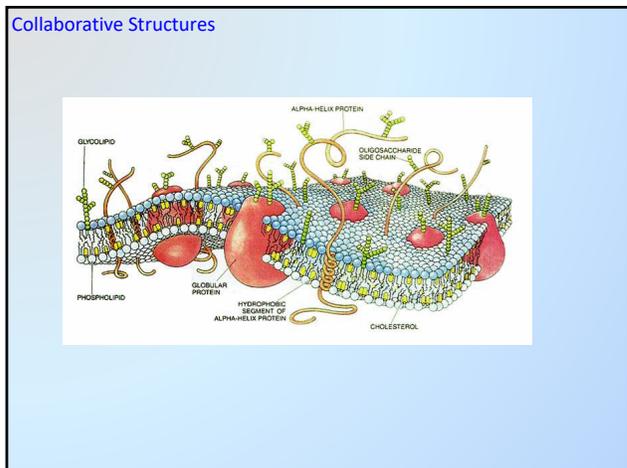
Collaborative Structures

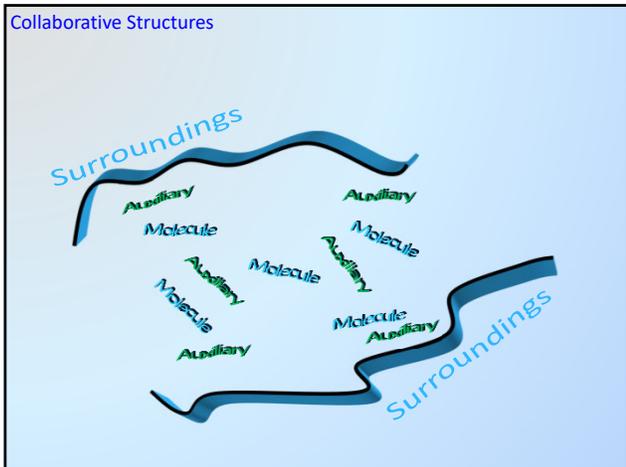


Collaborative Structures



Collaborative Structures





### Parkinson's/ALS Disease Therapeutic

Cc1c(C)c2c(c1)nc(C)c2N

**Cu ATSM**

**Increased Bioavailability**

**THE MICHAEL J. FOX FOUNDATION  
FOR PARKINSON'S RESEARCH**

Metal complexes and methods of treatment; Warner, John C.; Cheruku, Srinivasa R.; Hari, Anitha; Norman, James J.; Priority Date: November 11, 2013; US 2016/0271175; WO 2015/070177; EP 3068762; CA 2930290; CN 105899519.

### Hair Color Restoration

**FROM:** Keep away from children and pregnant women. Wash your hair daily. Do not use on children, pregnant women, or women who are breastfeeding. Read all directions and instructions.

**HAIRPRIN**

**RESTORES GRAY HAIR TO ITS TRUE COLOR**

Formulation and processes for hair coloring, continuation; Warner, John C.; Muollo, Laura; Stewart, Amie; Priority Date: October 14, 2013; US 9,522,102.  
Formulation and processes for hair coloring; Warner, John C.; Muollo, Laura; Stewart, Amie; Priority Date: October 14, 2013; US 8,826,100; WO 2015/057254; EP 3057561; JP 2016-033376; KR 2016-0089558; CN 105729729.

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## Pre-associative Reactivity

For over 180 years  
of "Modern Chemistry" ...

But Nature...

Heat things under high temperature

Runs reactions at "room" temperature

Apply high pressures

Runs reactions at ambient pressure

Use organic solvents

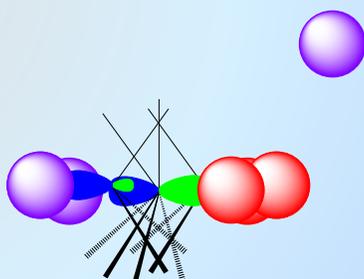
Uses water as a solvent

## Pre-associative Reactivity

*A thermometer is a  
molecular speedometer...*



## Pre-associative Reactivity



## Pre-associative Reactivity

*There is almost never a  
reactive collision in  
Nature!*

### Low Temperature Formaldehyde Free Wood Composites

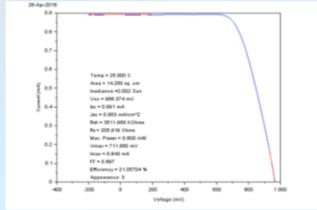


“Lignocellulosic Compositions and Methods of Making Same” Warner, John C.; Whitfield, Justin R.; Gladding, Jeffery A.; Allen, Richard M., US Patent Filed May 26, 2015

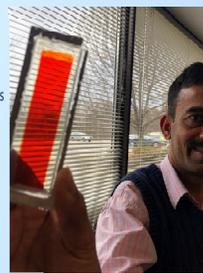
Lignocellulosic composites and methods of making same. Warner, John C.; Whitfield, Justin R.; Gladding, Jeffery A.; Allen, Richard M., Priority Date: May 26, 2016, US 2018/0147824, WO 2016/191521, EP 3302969, CA 2986427, JP 2018516784.

### High Performance, Printable, Copper Based Solar Cells

- Record voltage at all indoor light levels outperforming GaAs solar cells
  - >1 V at 1000 lux indoor light
  - Stable electrolyte system
- Strong portfolio of patent applications covering various aspects of material and process chemistry
- Multi-colored product opportunity
- Power density from stable device exceeds the performance of GaAs solar cell



28-Aug-2018  
 Temp = 28.0000 C  
 Area = 14.2000 cm<sup>2</sup>  
 Irradiance = 417.0000 W/m<sup>2</sup>  
 Voc = 0.99731444 V  
 Isc = 0.02010000 A/cm<sup>2</sup>  
 Jsc = 0.283380000 W/cm<sup>2</sup>  
 Rsc = 200.0000 Ohm  
 Min. Power = 0.00000000 W/cm<sup>2</sup>  
 Voc<sub>max</sub> = 1.110000 V  
 Isc<sub>max</sub> = 0.000000 A/cm<sup>2</sup>  
 FF = 0.8000  
 Efficiency = 11.000000 %  
 Approximate 3

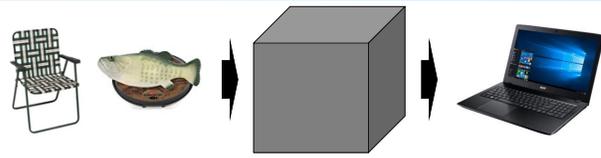



Solar cell dyes for copper redox based dye sensitized solar cells and combinations thereof. Warner, John C. et al., Priority Date: July 10, 2018, US Provisional 62/696,010.  
 Copper redox based dye sensitized solar cells. Warner, John C. et al., Priority Date: September 21, 2018, US Provisional 62/734,511.  
 Silibine and fused silibine derivatives as solar cell dyes. Warner, John C. Priority Date: May 9, 2017, US Provisional 62/703,645, WO 2018/208712.

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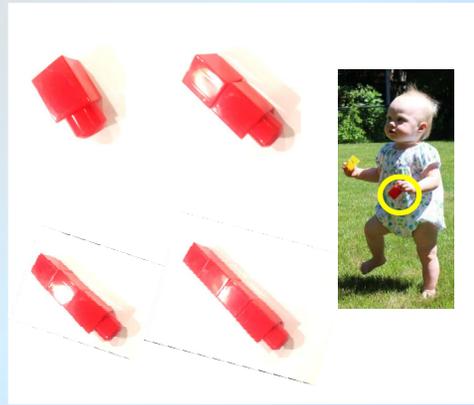
### Synchronous Orthogonal Mechanisms

Synchronous Orthogonal Mechanisms



Synchronous Orthogonal Mechanisms



Synchronous Orthogonal Mechanisms

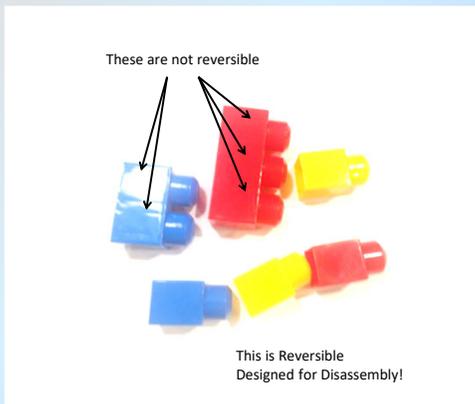


Synchronous Orthogonal Mechanisms

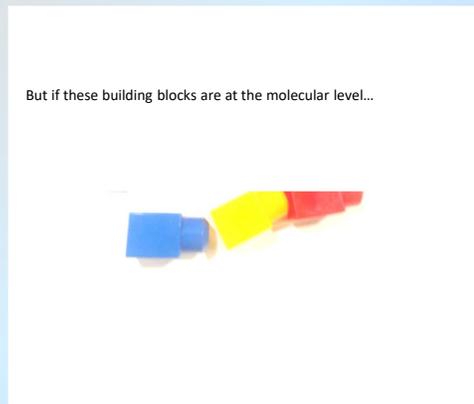


The introduction of a NEW building block is a game changer.

Synchronous Orthogonal Mechanisms



Synchronous Orthogonal Mechanisms



Synchronous Orthogonal Mechanisms



Synchronous Orthogonal Mechanisms



### Synchronous Orthogonal Mechanisms

**Elastin**

**Desmosine Crosslink**

### BPA Free Can Lining

**SAMHWA**

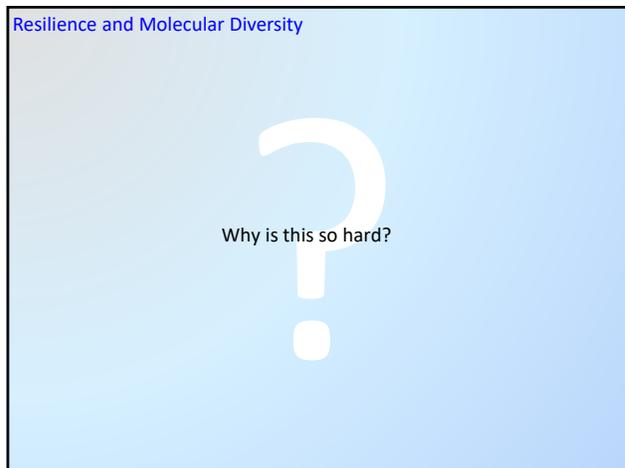
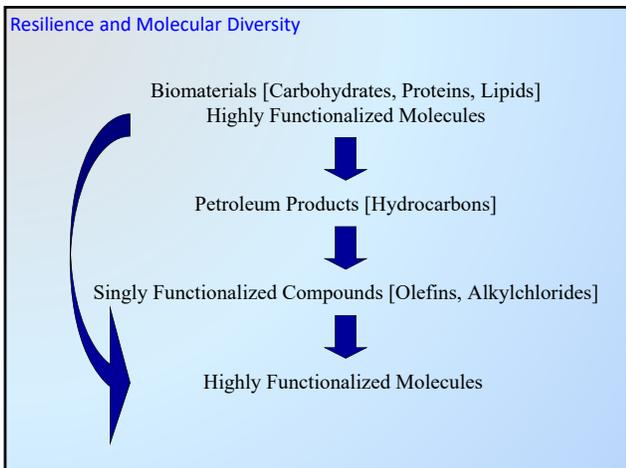
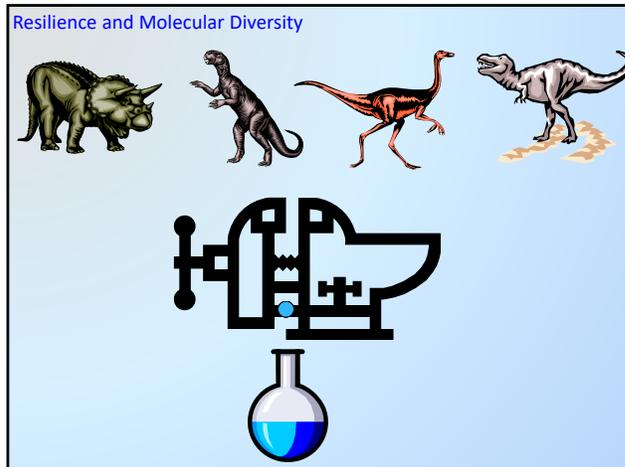
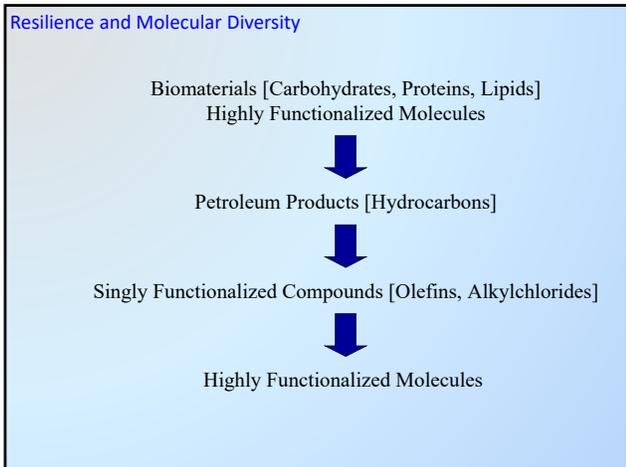
Bi-phenol-A free crosslinked polymer compositions. Warner, John C., Whitfield, Justin, Kearney, Frederick R., Gladding, Jeffrey, Hari, Anitha, Priority Date: June 27, 2016. US Provisional 62/355,074, WO 2016/005430.

### Photo Osmotic Desalination

**U.S. DEPARTMENT OF ENERGY**

Reversibly switchable surfactants and methods of extracting natural products, coating surfaces, cleaning laundry, and osmotic extraction using same. Warner, John C.; Cheruku, Srinivasa, Priority Date: June 23, 2016. US Provisional 62/553,805, WO 2017/223413.

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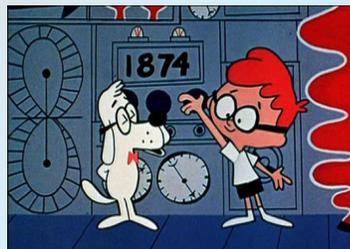


Resilience and Molecular Diversity

Biobased materials are easily synthesized...

...but extremely difficult (expensive) to purify

Resilience and Molecular Diversity



Resilience and Molecular Diversity

Designing systems based on high purity is a trap!

Locking the system into narrow and demanding process conditions.

Nature doesn't do this.

Nature designs *using* molecular diversity.

Resilience and Molecular Diversity



"Fluid Cell Membranes"

### Resilience and Molecular Diversity

A biobased process that creates a product with a diversity of components can be valued in its mixed form.

As long as the process is reproducible at commercial scale.

By valuing the unique diversity of a biobased process:

Your manufacturing is cost effective.

Your product has a higher value than the synthetic counterparts

### Ocean Plastics Recycling and Reclamation

June 29, 2015

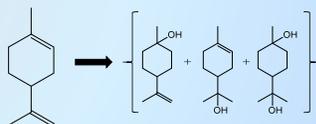


<http://www.parley.tv/updates/2015/7/3/adidas-x-parley>

<https://www.maritime-executive.com/article/adidas-uses-ocean-plastic-in-shoe>

<https://techcollective.com/news/2015/07/parley-adidas-ultra-boot-recycled-seawater-plastic>

### Electronics Recycling and Reclamation



LiCoO<sub>2</sub>

Method for the recovery of lithium cobalt oxide from lithium ion batteries. Poe, Sarah L.; Paradise, Christopher L.; Muollo, Laura R.; Pal, Reshma; Warner, John C.; Korzenski, Michael B., Priority Date: June 21, 2011, US 9,972,830, WO 2012/77620, EP 2724413, JP 2014526953, KR 20140039302, CN 103620861.

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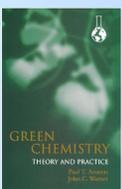
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**ENVR E-158A Green Chemistry**  
**Harvard Extension School**  
JohnWarner@FAS.Harvard.Edu  
Spring 2019: Online  
Wednesdays 7:20-9:20 PM



 [John.Warner@WarnerBabcock.com](mailto:John.Warner@WarnerBabcock.com)  [@JohnWarnerOrg](https://twitter.com/JohnWarnerOrg)