Developing Nanometer Scale, Atomically Precise Metallo-Catalysts with Molecular Lego

Contract Number EE0008321
Schafmeister Group/Partner Organizations
8/15/2018-8/14/2020

Christian Schafmeister – Temple University

U.S. DOE Advanced Manufacturing Office Program Review Meeting
Washington, D.C.
June 12, 2019

One of five coordinated 1465 FOA projects in Atomically Precise Manufacturing

Overview

Project Title: **Developing Nanometer Scale, Atomically Precise Metallo-Catalysts with Molecular Lego**

Timeline:

Project Start Date: 08/15/2018

Budget Period End Date: 08/14/2020

Project End Date: 08/14/2020

Project Budget and Costs:

Budget	DOE Share	Cost Share	Total	Cost Share %
Overall Budget	$795,834	$198,957	$994,793	20%
Approved Budget (BP-1&2)	$795,834	$198,957	$994,793	20%
Costs as of 3/31/19	$143,475	$63,324	$206,799	30%

Barriers and Challenges:

- Synthesis of highly pre-organized macromolecules (3,000 to 5,000 Daltons) containing catalytic Lewis acid metal sites. Compared with macromolecules made to date.
  - Scale up of building block synthesis (10x).
  - Scale up the size of catalyst (5x).
- Demonstrate stereocontrolled polyester synthesis by molecular Lego catalysts.
- Broad scope: stereocontrolled olefin epoxidation, C-H activation and atomically precise membranes for purification of olefin feedstocks - all based on molecular Lego nanostructures.

AMO MYPP Connection:

- 5.4.2: Atomically precise catalysts with 10,000x selective catalytic improvement (compared to the state of the art) for recyclable plastics.
- 5.4.3: Sustained program to design and construct atomically precise catalysts and filters for manufacturing.

Project Team and Roles:

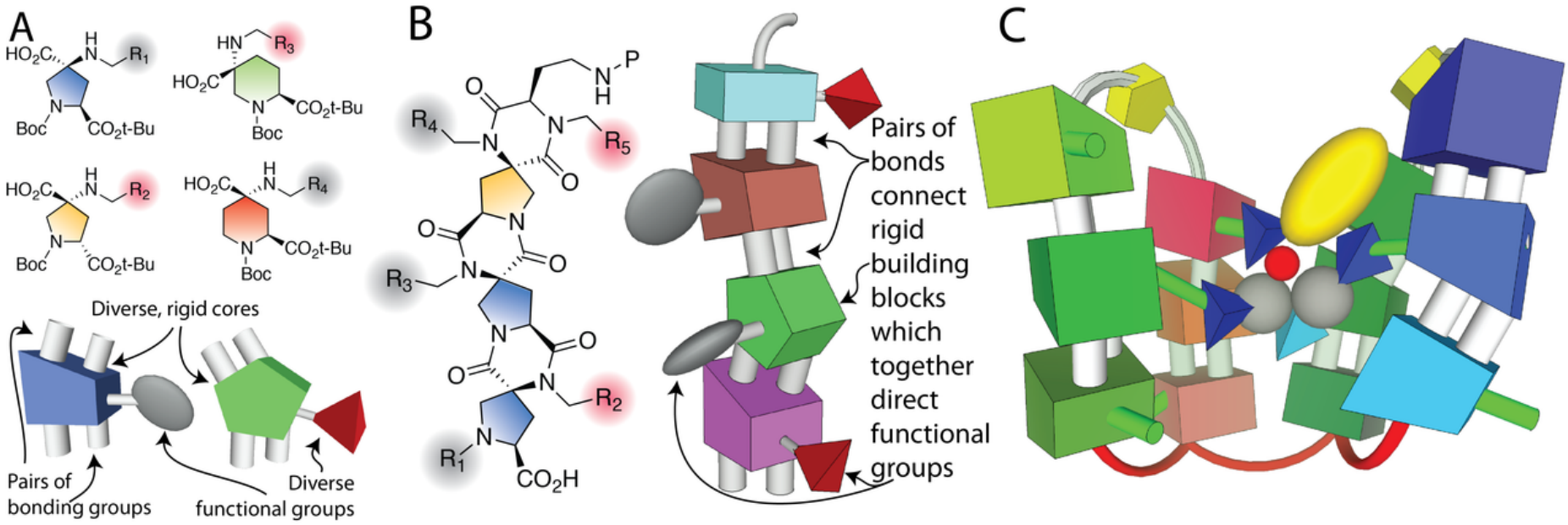
- Schafmeister group (Chemistry@Temple) has invented molecular Lego nanostructures and demonstrated catalysis and is developing Cando software to design molecular Lego nanostructures for industrial applications.
- Dobereiner group (Chemistry@Temple) experts in organometallic chemistry, polymers and characterization of catalysts.

Project Objective(s)

- Develop atomically precise, large, enzyme-like molecules that contain structured catalytic metal sites that are 10,000x more active/selective than current catalysts = big energy savings.
- Achieve catalysts on the nanometer scale that assemble advanced bulk materials (polyester) on the macroscopic scale.
- These catalysts create polyester polymers with excellent material properties (clear, strong) at ambient temperature. Replace polyolefins. Enable circular economy. Eliminate purification.
- Catalysts are ultimate "Green Chemistry" – Lower manufacturing energy use. Enable recycling. **Prevent toxic microplastics.**
- Difficult because requirements are:
  - Modular, molecular Lego-based catalysts 5x larger (>3,000 Daltons) than before.
  - Scaled up molecular Lego synthesis scale (10x).

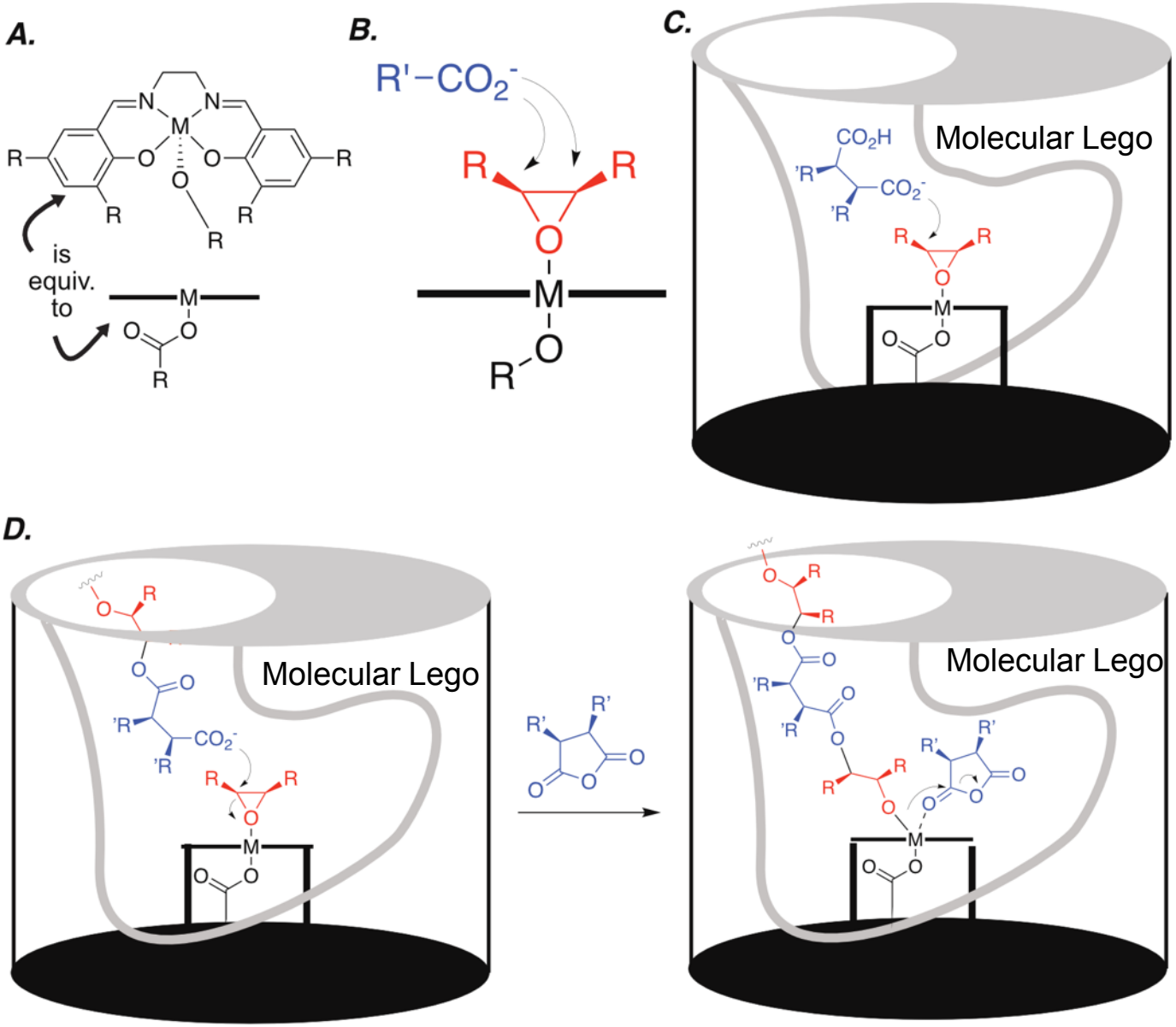
Technical Innovation

- **Current catalysts** are materials or small molecules with **poorly controlled active sites**.
- Our **molecular Lego "second shell"** around the metal center will combine the **selectivity of enzymes** – with the **rugged nature** of inorganic material catalysts.



Molecular Lego assembly stages

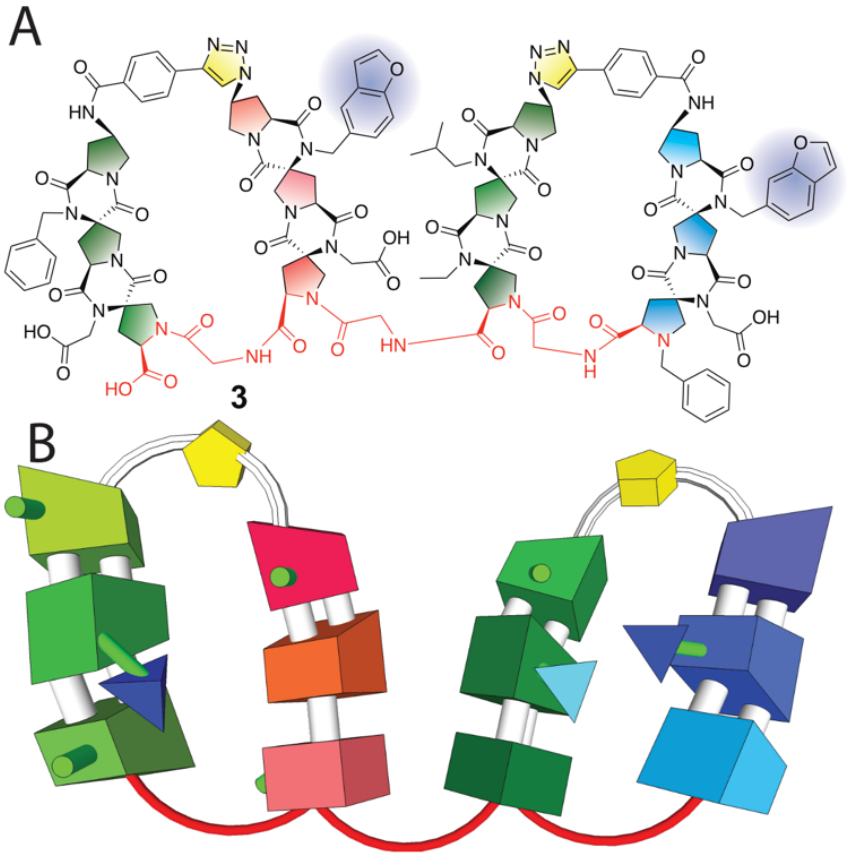
Technical Innovation

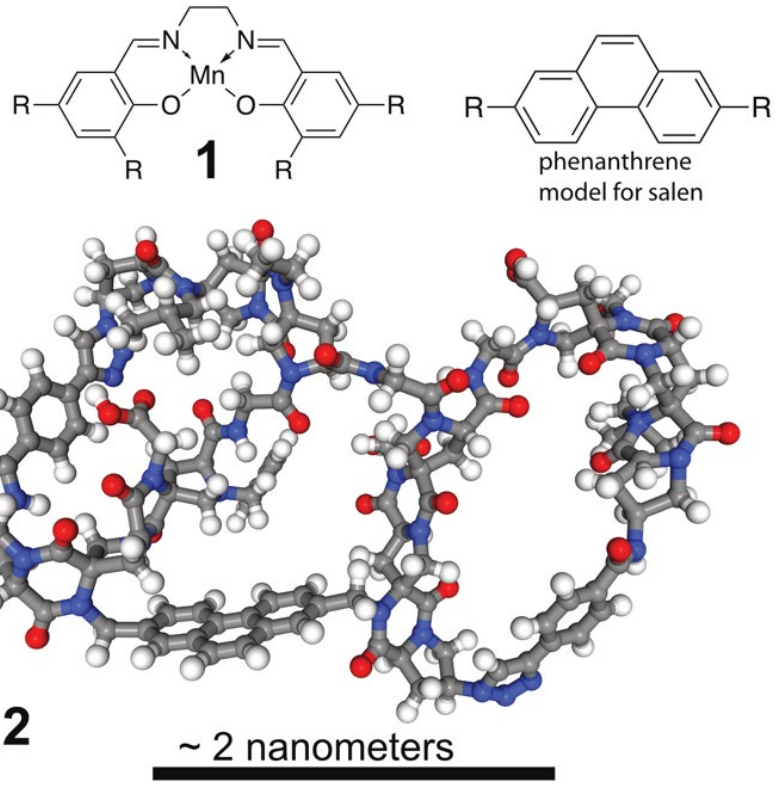


Our catalysts (cartoon) are just 10x larger than current catalysts and will create enzyme-like pockets that control substrate geometry.

Technical Approach

- Development of macromolecular metal binding catalysts wherein the scaffold will control polyester formation. Use computational design with Cando.

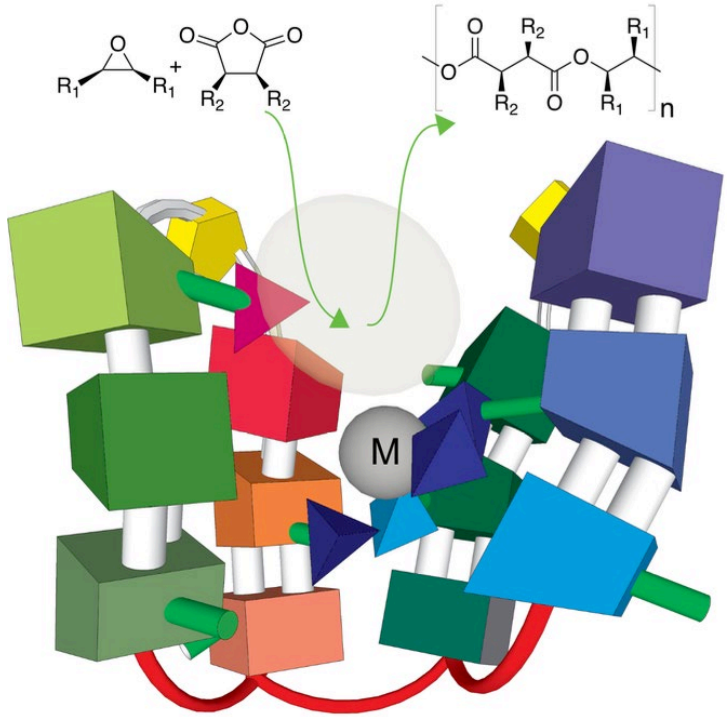




Technical Approach

- We synthesize 200 Dalton sized building blocks, assemble them into 1,000 Dalton nanostructures and assemble those into 3,000 Dalton molecular Lego nanostructures displaying atomically precise pockets and metal binding sites.

- We are scaling up the size and amount of molecular Lego catalysts.
- Schafmeister group (Chemistry@Temple) invented molecular Lego nanostructures and demonstrated catalysis and design software.
- Dobereiner group (Chemistry@Temple) are experts in organometallic chemistry.



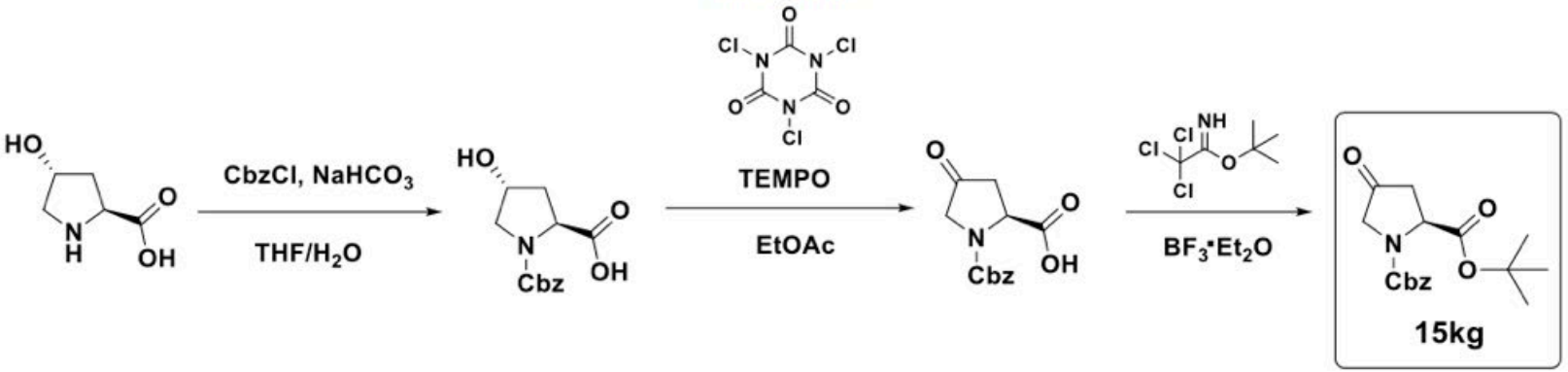
Cartoon of APM polyester catalyst

Results and Accomplishments

- Scaled up (by 78x) monomer synthesis to multi kilogram scale.
- Scaled up (by 10x) molecular Lego segment synthesis to hundred milligram scale.
- Milestone achieved: three molecular Lego, chromium salen catalysts and demonstrated that they carry out polyester polymerization.
- Milestone achieved: Demonstrated analytical chemistry for characterization of catalyst made polyester.
- Goal for the next year: Assemble chromium salen complexes inside of pockets large enough to demonstrate enantioselective polyester production.

Results and Accomplishments

10 kilogram contract synthesis of molecular Lego intermediate (78x scale)

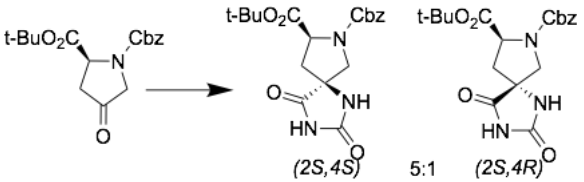


10 kg of ketone, the 4th intermediate of the 7 step building block synthesis

Results and Accomplishments

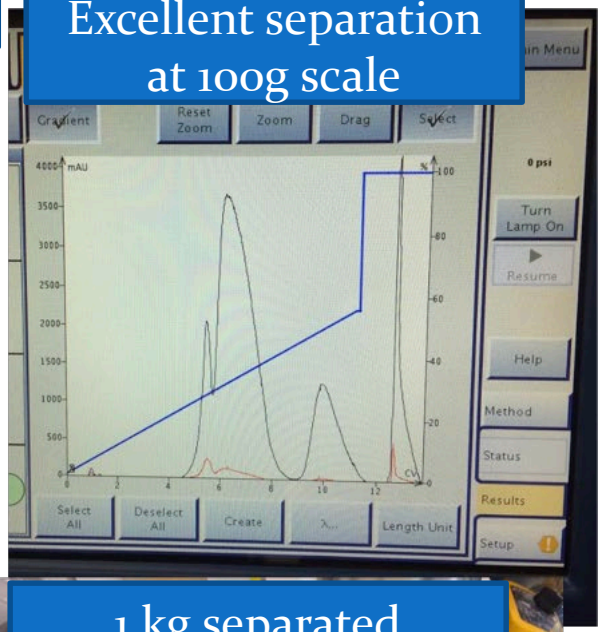
1 kilogram scale (5x scaleup) of building block synthesis and purification

Further processing to building blocks

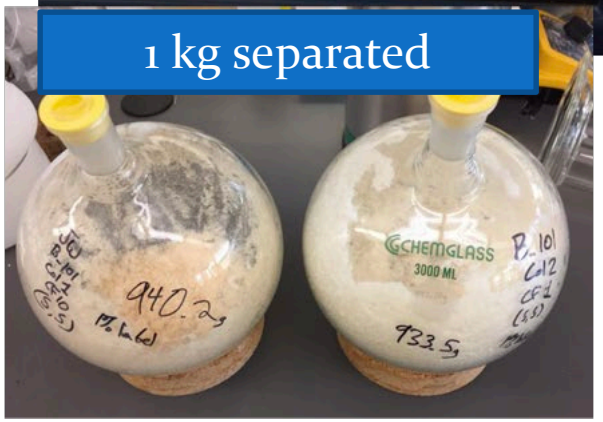


Chromatography

Excellent separation at 100g scale

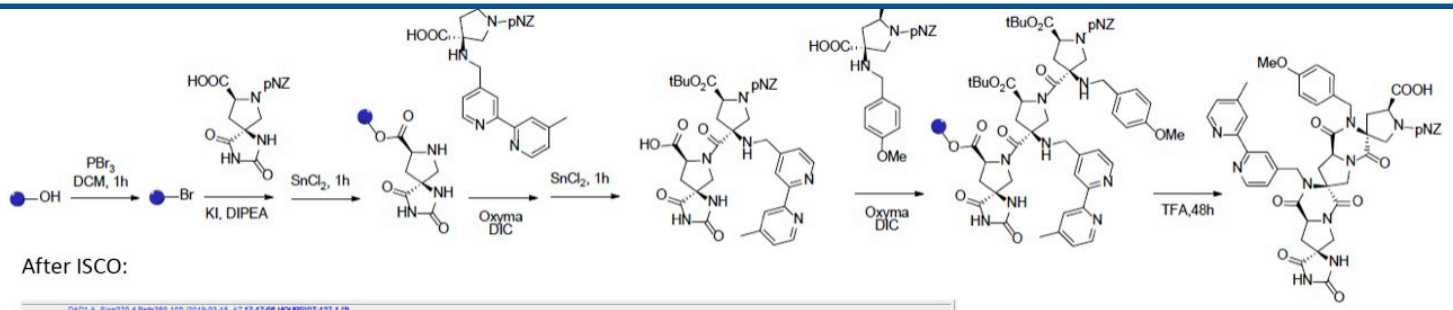


1 kg separated

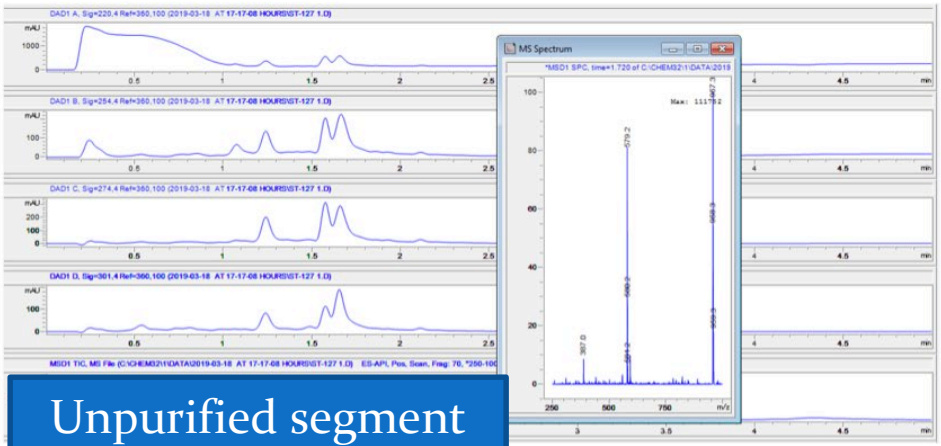


Results and Accomplishments

Hundred milligram (10x increase) in molecular Lego segment synthesis

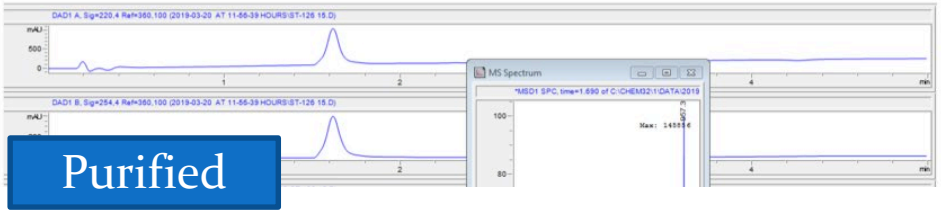


After ISCO:



Unpurified segment

After HPLC (100 mg):



Purified

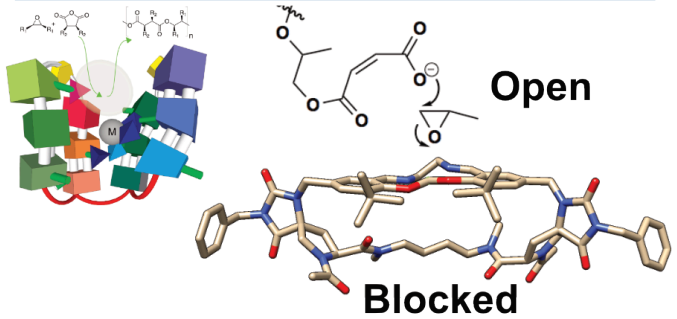
M.W.: 956.31

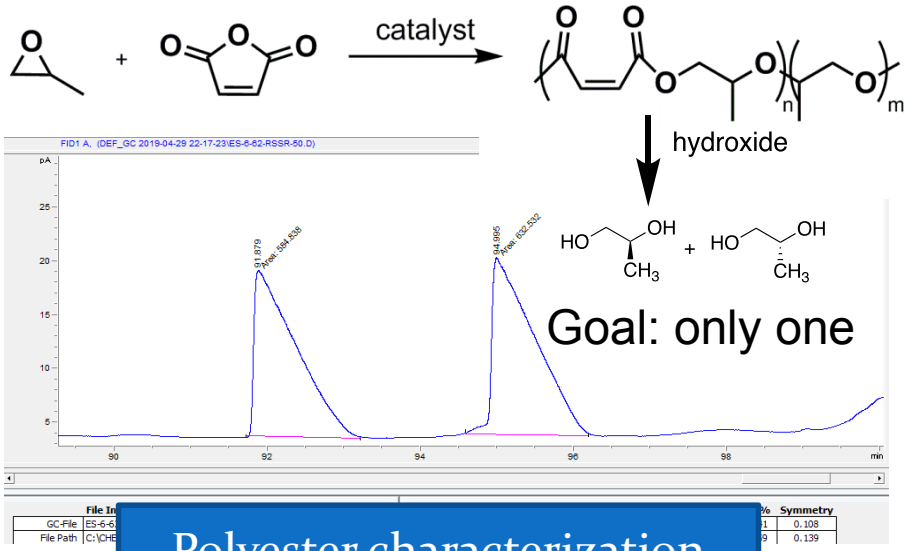
Chromatography

Results and Accomplishments

Year 1 Milestone achieved: three molecular Lego catalysts that form polyester

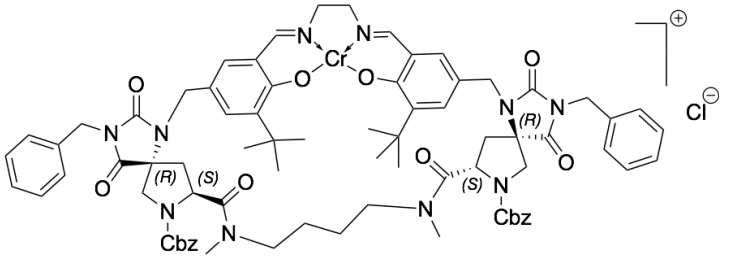
Gen 1 catalyst design



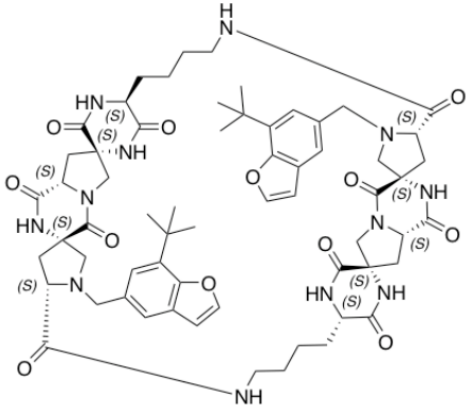


Polyester characterization

One of three gen 1 catalysts



Cation portion:
Chemical Formula: $C_{76}H_{84}CrN_{10}O_{12}$
Exact Mass: 1380.5675



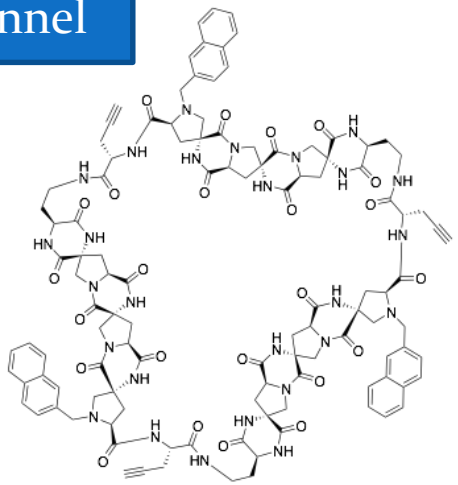
Chemical Formula: $C_{62}H_{76}N_{12}O_{12}$
Exact Mass: 1180.5706

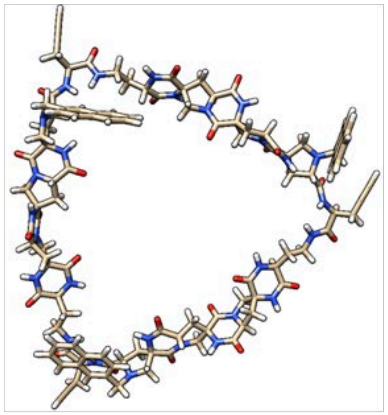
Gen 2 catalyst

Results and Accomplishments

Related project: (AMO supported) creates pores for atomically precise filtration – these pocket molecules are prototypes for polyester catalysts

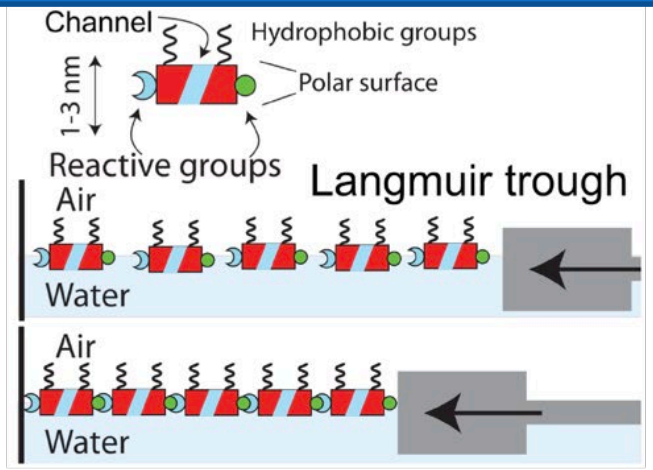
Gen 1 AP channel

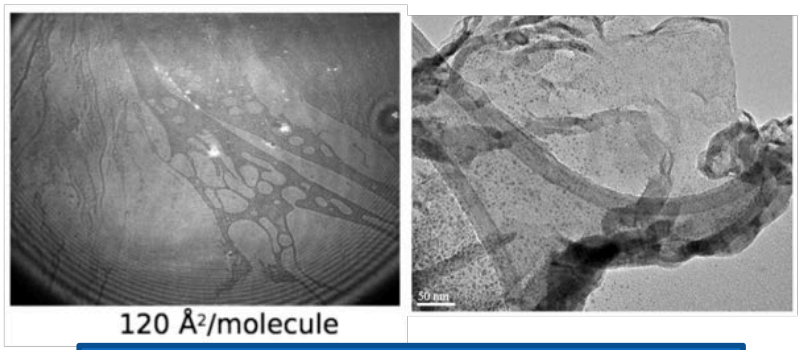




1 gram = football field membrane

Self assembly of AP membranes





Membranes of AP channels

Transition (beyond DOE assistance)

- We have started a company (ThirdLaw LLC) to commercialize Cando software to design molecular Lego nanostructures for drug discovery and atomically precise membranes.
- We are collaborating with four drug discovery companies to enhance and commercialize our software.
- I have started a second venture to commercialize molecular Lego based APM for new diagnostics, catalysts, membranes and sensors.
- In discussion with with oil and polymer companies.
- Strategy: Demonstrate active/selective molecular Lego catalysts/membranes, patent, then license to industry.
- Awarded 2019 DOE SBIR/STTR to *develop atomically precise, energy efficient membranes assembled from "Molecular Lego" to separate hydrocarbon mixtures*.