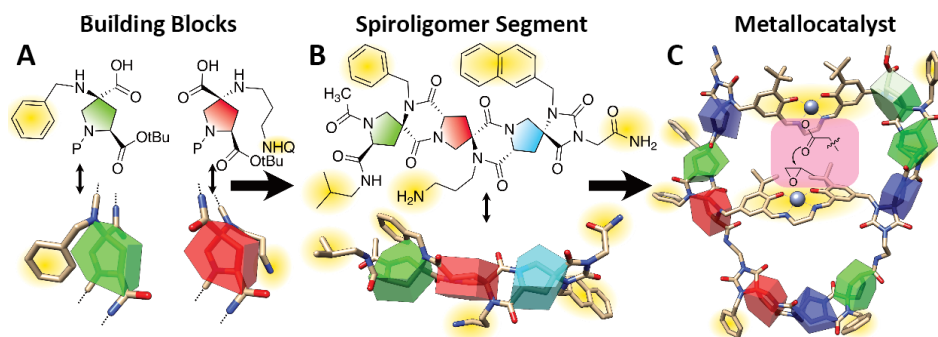


Developing Nanometer-Scale, Atomically Precise Metallo-Catalysts with Molecular Lego

Atomically precise manufacturing (APM) is an emerging disruptive technology that could dramatically reduce energy use and increase performance of materials, structures, devices, and finished goods. Using APM, every atom is at its specified location relative to the other atoms—there are no defects, missing atoms, extra atoms, or incorrect (impurity) atoms. Like other disruptive technologies, APM will first be commercialized in early premium markets, such as pharmaceutical chemical production.

New atomically precise (AP) catalysts designed for specific processes could dramatically reduce the energy and environmental impact of the chemical industry. This project is aimed at AP catalysts to manufacture environmentally friendly polyesters that can cost-effectively compete with polyolefin plastics, the dominant plastic material used worldwide. Polyolefin plastics are manufactured via polymerization processes using industrial catalysts at high temperatures. Polyolefin products do not degrade and have become a major environmental disposal problem worldwide. The ‘artificial enzymes’ that will be created in this project are highly selective (hence, use far less energy)



Molecular Lego can be assembled into a catalyst that dramatically accelerates production and increases the yield of a biodegradable polyester plastic. Green and red building blocks show different shapes (stereochemistry). Yellow side-chains are the chemical tools (functional groups) that come with each building block. A key feature of the Lego is the pairwise (amide) bonding that makes the catalyst robust. In (A) bottom, dotted lines indicate where building blocks join in (B) forming pairs of bonds that provide stiffness to the spiroligomers and point the yellow molecular tools to where specific catalytic reactions take place. In (C), a 3D Lego metallo-catalyst made of spiroligomer segments is shown. The magenta square highlights one step of polyester formation.

Graphic image courtesy of Temple University

and would make polyesters that are biodegradable. The key innovation is that the ‘molecular Lego’ could form a robust catalyst that is as selective as enzymes and enables once-through processing.

The AP catalysts will be assembled from AP shape-programmable macromolecules called spiroligomers. The spiroligomers are designed and constructed from synthetic, cyclic, stereochemically pure (same shape) bis-amino acid building blocks. The building blocks and the spiroligomer segments created from them (molecular Lego) will be assembled into AP nanometer-scale macromolecules. In this project, the macromolecules are metallo-enzyme catalysts for polymer production. The controlled geometry of these metallo-enzyme catalysts improves activity and selectivity. An existing software package will be used to rapidly search potential spiroligomer sequences and identify candidate catalysts that will make the most stereospecific polyester polymers at the lowest cost.

Benefits for Our Industry and Our Nation

Catalysts are a vital technology for transforming materials into valuable chemicals. By advancing novel catalysts, many petrochemical industry processes would be able to operate at lower

temperatures and eliminate many process steps, thereby reducing energy use and costs. The specific tailored approach envisioned in this project may be able to boost catalytic activity for polyester polymerization up to 1,000 times, resulting in an estimated energy intensity reduction of approximately 50%. In addition, the more environmentally friendly products made with these catalysts will dramatically reduce plastic pollution.

Applications in Our Nation’s Industry

AP catalysts could be developed for many industrial applications. By coupling AP Legos (spiroligomers) with advanced software and modeling, this project is developing a holistic and accelerated catalyst development approach that is a fundamental rethinking of the traditional empirical (trial-and-error) based approach to developing catalysts. While the initial focus is on polyolefins, many petrochemical industries use catalysts to accelerate or enhance desired chemical reactions. Other potential applications with significant opportunities for energy and cost savings include water splitting for use in hydrogen fuel cells and ammonia production for fertilizer.

Project Description

The project objective is to demonstrate highly energy efficient, scalable bottom-up production of plastics that previously have only been made using energy intensive top-down methods. The AP catalysts would enable production of aliphatic, stereospecific polyester polymers. Initially, the project will develop Lewis acid-based catalysts with nanoscale control over the formation of aliphatic polyesters. Multiple spirologomer Legos will be assembled into AP nanometer-scale metallo-enzyme catalysts to enable stereospecific polyester polymer production. Approximately a dozen macromolecular catalysts will be designed, synthesized, and characterized. Building on a previously developed computer-aided nanostructure design and optimization (CANDO) software package, the researchers are exploring different chemical reactions, protective groups, and attachment groups that can be used to assemble spirologomers. This software considers the molecular mechanics of Legos that comprise the active sites, and it will be used to rapidly search millions of spirologomer sequences.

Barriers

- Reliably manufacturing spirologomers at commercial scale, including methods that allow robotic synthesizers; efficient production of large spirologomer structures requires many chemical steps that all need to be highly efficient, coordinated, and sequenced
- Designing the large spirologomer catalyst structures so that they carry out the desired catalytic function; experimental data is needed to teach CANDO software to make better design predictions

Pathways

To develop AP metallo-catalysts that accelerate specific polymerization reactions, a five-step catalyst development workflow process will be utilized: 1) design of active sites; 2) design of spirologomer segments that include those active sites; 3) synthesis of spirologomer building blocks; 4) synthesis of spirologomer segments; and 5) assembly of spirologomer segments into macromolecular metallo-salen catalysts.

Both CANDO software and experimental design will be used. Two to eight catalysts will be synthesized to demonstrate the catalyst design and synthesis workflow. Subsequently, up to six additional candidate catalysts will be synthesized and characterized through a series of intermediate synthesis and purification steps that build toward functionalized bundles of spirologomers. Finally, the resulting macromolecular catalysts will be screened and evaluated for their activity and selectivity.

Milestones

This two-year project began in August 2018:

- Demonstrate catalyst design and synthesis workflow by designing, synthesizing, and characterizing at least two spirologomer-based metallo-salen catalysts (completed)
- Synthesize at least six additional metallo-salen catalysts (2020)
- Assess synthesized metallo-salen catalysts to confirm performance metrics, such as catalytic activity, exceed performance of existing catalysts (2020)

Technology Transition

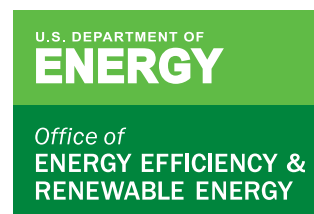
As knowledge is acquired throughout this project, Temple University will explore potential licensing to industrial partners. To further advance the technology, Temple researchers formed a spinoff company for molecular Lego and software development—called ThirdLaw—in 2019. The company is developing the CANDO software for use in designing molecular Lego and therapeutic compounds for the pharmaceutical industry. The controlled catalytic pockets that can be created using molecular Lego will allow the formation of exceptionally pure enantiospecific products, a requirement of modern therapeutics. ThirdLaw will develop molecular Lego for other applications in catalysis and membranes for separations. To commercialize products, ThirdLaw will also partner with industrial end users to design purpose-built catalysts for specific reactions in order to improve yield and selectivity. This tailored approach to catalyst design and use is expected to be groundbreaking and draw significant interest from U.S. industry.

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