Bio-inspired Light-Escalated Chemistry (BioLEC)
EFRC Director: Gregory Scholes
Lead Institution: Princeton
Class: 2018 – 2026

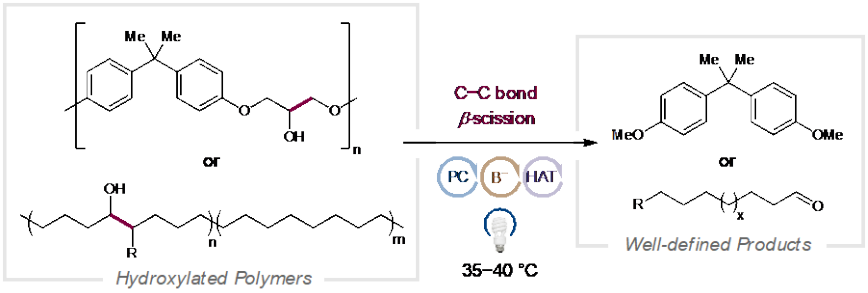
Mission Statement*: To combine light harvesting and solar photochemistry to enable more powerful editing, building, and transforming of abundant materials to produce energy-rich feedstock chemicals.*

The search for more efficient, cost-effective, and green manufacturing technologies is of paramount importance. Chemical manufacturing accounts for 10% of total global energy consumption and is responsible for 7% of the world's greenhouse gas emissions. Fossil fuels remain the most widely employed source of energy to generate the high temperatures and pressures required to manufacture chemicals, and are often also used as starting materials for production. Solar energy can be converted to chemical energy when used to excite light-absorbing catalysts in chemical syntheses in a manner akin to that of photosynthesis, and transformation of abundant biomass to feedstock chemicals could alleviate the need for non-renewable sources; BioLEC aims to tackle both these challenges.

In contrast to traditional synthetic routes, photoredox catalysts utilize light to drive reactivity under very mild conditions. These methodologies have been mostly employed in the synthesis of small molecules such as pharmaceuticals, and are yet to be translated into mass production of feedstock chemicals. Photocatalytic methods, though highly efficient and mild, proceed via intricate mechanisms that are not easily applicable in broad scope large scale reactions. Translating these technologies to a wider range of chemical manufacturing applications therefore requires new approaches that make the reaction steps more robust and more efficient, as well as the underlying mechanistic knowledge to target these steps.

Since launching in August 2018, BioLEC has made significant advances on multiple fronts: in understanding what drives photoredox catalysis at a mechanistic level to enable the design of new improved catalysts; in taking inspiration from photosynthesis to tackle kinetic, efficiency and specificity shortcomings in traditional photocatalysts, such as obviating the low absorption cross-section limitation of organometallic photocatalysts using energy transfer from light-harvesting systems; in using light to manipulate enzymes for innovative photochemistry; and in employing photocatalysts for novel reactions for energy applications, such as light-driven recycling of polymers to reusable monomer building blocks, and the contrathermodynamic photocatalytic isomerization of internal olefins to more reactive terminal olefins. As we enter this second phase of our center, we will advance towards our goals through three thrusts:

A: Develop innovative photochemistry that enables new routes for synthesizing chemical feedstocks
We will develop new photochemistry and feedstocks in BioLEC, and expand the scope of mechanistic tools and reactive substrates available to the photocatalysis community. Drawing on the rich physical chemistry capabilities in BioLEC, new photochemical techniques for reactivity and experimental characterization will be developed. New reactivities will push the boundaries of photoexcitation and accessible

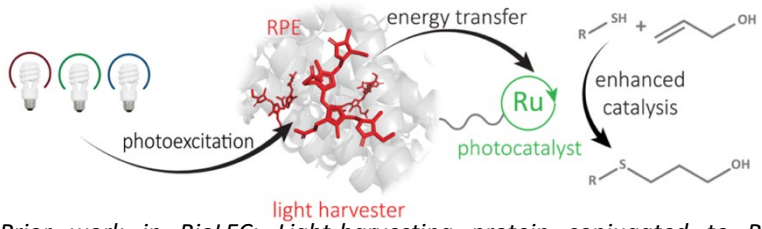


Prior work in BioLEC: photo-driven depolymerization of thermoplastics, enabled by light-driven O–H proton-coupled electron transfer. Approach is compatible with insoluble polymers and involves no stoichiometric reagents.

redox potentials. Finally, this new chemistry will valorize feedstocks that were previously inaccessible to photochemistry, providing a pathway toward recycling waste.

B: Discover, synthesize, and study photoenzymes that enable enhanced catalysis

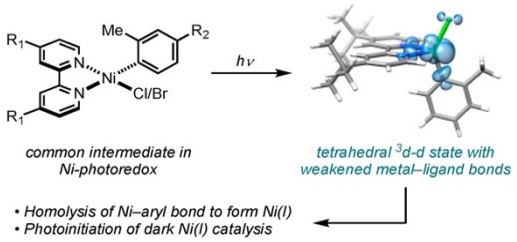
BioLEC's work transforming enzymes' catalytic abilities with light provides not only innovative functionality but also key insights into the fundamental functions of the microenvironment within the protein. By designing microenvironments in photoactive proteins, or "photoenzymes", we will introduce functionality that first mimics and then exceeds that of natural systems. Additionally, bioinspired tactics from photocatalysis involve separating catalytic functions to improve efficiency or selectivity.



Prior work in BioLEC: Light-harvesting protein conjugated to Ru photocatalyst generates increased yields and makes reactions at previously unusable irradiation wavelengths possible.

C: Inform design of photocatalysts by elucidating photocatalysis mechanisms

In the first phase of BioLEC we advanced fundamental knowledge of the elementary organometallic steps available through visible light excitation by applying a variety of physical techniques (e.g., transient absorption spectroscopy, organometallic synthesis, EPR, pulse radiolysis, ultra-fast IR) to study the mechanisms in multiple metallaphotoredox reactions, including C–O, C–N, and C–C couplings. We will build on these efforts with the goal of gaining a more global understanding of how changes to substrate, ligand, and photocatalyst identity affect the reaction mechanism. We will focus on using this understanding to design improved and new dual transition metal/photoredox coupling reactions.



Prior work in BioLEC: Ni(II) excited states relevant to Ni-photoredox catalysis

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