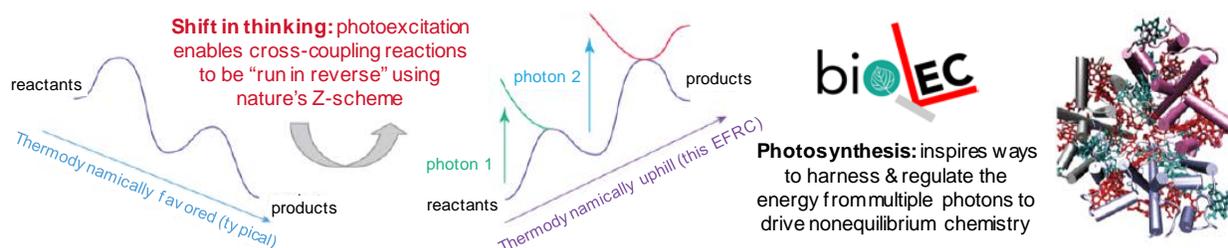


**Bioinspired Light-Escalated Chemistry (BioLEC)**  
**EFRC Director: Gregory Scholes**  
**Lead Institution: Princeton University**  
**Class: 2018 – 2022**

**Mission Statement:** *To employ light harvesting and advances in solar photochemistry to enable unprecedented photoinduced cross-coupling reactions that valorize abundant molecules.*

The energy input required to transform stable and abundant molecules to valuable products is greatly reduced by the use of catalysts. A fundamental aim in catalysis is to devise new ways to convert plentiful and unreactive molecules for energy-relevant applications. The research proposed for the BioLEC Energy Frontier Research Center (EFRC) will expand our understanding of fundamentals of solar photochemistry and photosynthetic systems to enable sophisticated cross-coupling chemistry powered by light, Figure 1. The resulting breakthroughs will yield energy-relevant chemicals, fuels, and materials. At the frontier of this endeavor, we aim to catalyze reactions that have prohibitive energy barriers for equilibrium chemistry—reactants are more stable than products. The reactions that we target are presently inconceivable using the leading edge of modern synthetic chemistry. Our approach is inspired by the way that nature combines the energy of multiple photons to ramp up redox capability beyond that achievable with the energy from a single photon. To succeed, BioLEC unites scientific communities that rarely interact—organic synthesis, structural and molecular biology, and physical chemistry.

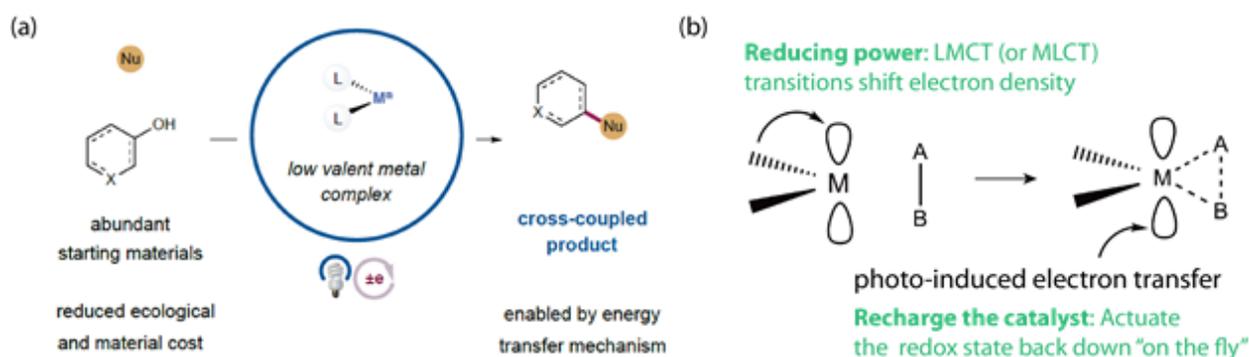


**Figure 1.** BioLEC's interdisciplinary approach will enable nonequilibrium chemistry.

The BioLEC EFRC strives to achieve a profound understanding of solar photochemistry and photosynthetic systems to enable photoinduced cross-coupling chemistry to create valuable chemicals, fuels, and materials. Our research approach to developing photocatalysis capable of creating valuable chemicals from abundant molecules is organized within four research thrusts. In Thrust A (Lead: Abigail Doyle), we develop new single-electron-transfer photoinduced cross-coupling systems, reveal how photoexcitation increases their potency, and connect these catalysts to light-harvesting antennas. We understand the fundamental photophysics of high electrochemical potential generation for photocatalytic reactions; devise sophisticated new mechanisms to harness the energy of multiple photons and multielectron transfers to actuate redox states in Thrust B (Lead: Garry Rumbles). We elucidate photophysical mechanisms by which photosynthetic proteins use light harvesting as a distribution hub for excitation energy in Thrust C (Lead: Gabriela Schlau-Cohen) and design biohybrids that function as biocatalysts for high-energy chemistry. The molecular insights obtained from Thrusts A – C will be utilized to design and demonstrate photoinduced cross-coupling reactions using the combined energy of multiple photoexcitations to drive chemical reactions that are prohibitively disfavored at equilibrium in Thrust D (Lead: David MacMillan). In particular, we target bond activation by organometallic catalysts to produce chemical feedstocks and fuels.

In the past half-century, transition metal catalysis has arisen as a uniquely enabling platform for molecular construction. The development of *cross-coupling* technologies, wherein aryl or alkyl substrates can be forged together, have proven to be particularly powerful for the rapid construction of complex molecular frameworks from modular building blocks. Simply put, these reactions enable the attachment of two molecular units A and B to form the new molecule A–B, facilitated by organometallic reagents (Figure 2).

A common reactive precursor for cross-coupling technologies includes a carbon–halogen bond, because that bond is readily ‘activated’ (i.e. the functional group can be edited). However, production of this precursor requires energy-intensive synthesis and it generates hazardous waste. Chemical feedstocks should be readily transformable under current synthetic methods. For example, phenols and anilines are abundant, naturally occurring compounds that can be found in biomass feedstocks, but at present their functional groups (–OH or –NH<sub>2</sub>), unlike halides, are too strongly attached to the phenol ring to be activated. The sophisticated photoinduced cross-coupling chemistry reactions needed are currently inconceivable using today’s leading-edge synthetic chemistry. These challenges are being addressed by BioLEC. For example, we hypothesize that we can employ phenols and anilines as aryl halide surrogates in cross-coupling reactions, with oxidative addition activating the traditionally unreactive C–O and C–N bonds, respectively. That will be enabled by working out how to escalate the chemical reactivity of organometallic catalysts by using a combination of photo-excitation and photoinduced bimolecular electron transfers to yield nonequilibrium valence states ‘on the fly’ during the reaction.



**Figure 2.** (a) Activation of inert bonds for cross-coupling. (b) BioLEC will step-change the limits of equilibrium redox potentials by adding or removing electrons “on the fly,” thereby driving reactions forward.

Bioinspired Light-Escalated Chemistry (BioLEC)	
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