Theme 1
Energy Capture and Catalysis at the Nanoscale

**Grand Challenge:** Enhance the efficiency of solar energy capture in artificial (and natural) systems
Theme 1 Objectives

**Objective 1.** Define basic principles of natural photosynthetic solar energy capture, pigment organization and protection

**Objective 2.** Develop nanocomposite materials with enhanced charge separation and migration properties

**Objective 3.** Fabricate integrated natural and hybrid self-assembling biomimetic nanocomposite materials with efficient broad bandwidth energy capture capabilities
Theme 1

People: Cindy Berrie; Stefan Bossman; Viktor Chikan, Francis D’Souza; Daniel Higgins; Ryszard Jankowiak; Paul Rilemma; Mark Richter

Plus many collaborators
Objective 1
Define basic principles of natural photosynthetic solar energy capture

The long-term goal is to reach a fundamental and unified understanding of the ultrafast solar energy-driven primary events of photosynthesis as they occur in higher plants, cyanobacteria, purple bacteria and green algae.

Solar energy is converted with high efficiency into a trans-membrane electrochemical potential (or PMF) that is used for the oxidation of water to form oxygen and ATP synthesis.
Regulatory dissipation of excess excitation energy - photoprotection by non-photochemical quenching (NPQ), occurs at high values of proton motive force (pmf) which promote reorganization of the light harvesting complexes.

Can we mimic natural systems to create highly efficient artificial systems that can adapt to changing conditions of light quality and quantity?

Can we engineer plants and algae to increase photosynthetic efficiency?
Richter et al.,

The photosynthetic ATP synthase dictates the threshold pmf for NPQ activation.

Results: Gene/protein engineering studies of ATP synthase components have identified the likely molecular basis by which the ATP synthase senses the magnitude of the pmf and establishes the threshold for NPQ activation.
A critically-placed dithiol in the central rotating spindle (gamma subunit) of the ATP synthase regulates rotation, controls the conformation of the epsilon subunit which modulates the magnitude of the pmf which in turn governs NPQ.

- **Epsilon subunit**
- **dithiol**
- **D244K/E2446 mutations**
Redox titrations indicate no difference in midpoint potentials between wild type and mutant ATP synthases.

Loss of dilution-dependent epsilon subunit release by the 244K Mutant.

Colvert et al., 2011
Hypothesis: Threshold value of the pmf necessary to induce NPQ is directly controlled by the conformational state of the gamma and epsilon subunits of the photosynthetic ATP synthase by regulating \( H^+ \) slippage.
Using hole-burning spectroscopy to 1) identify the true excited state structure and electron transport dynamics of the natural Photosystem II core complex in higher and 2) identify mechanisms of excess energy dissipation in the light harvesting systems.

**Results:** Identified, for the first time, the optical properties of the intact reaction center in the PSII core. Emission from the charge-separating (CT) State in the PSII core has thus been identified.
Resonant and nonresonant hole-burned spectra clearly show that photoprotective energy dissipation in LHCII from plants involves a Chl-Chl charge-transfer (CT) state. We propose that this state is formed in LHCII oligomers, which are induced as part of the NPQ response.

R. Jankowiak et al. 2011, unpublished results
Objective 2

Develop nanocomposite materials with enhanced charge separation and migration properties
Cindy Berrie, Viktor Chikan, Paul Rilemma, Francis D’Souza

Identify the factors affecting electron transport at Interfaces in dye-sensitized solar cells

Optimization of preparation and characterization of TiO2 substrates for dye attachment; characterized model dye attachment to surfaces

Synthesis and characterization of transition metal dyes, primarily of Re(I), in Grätzel Cells.
**Chikan et al.** have successfully synthesized new bare CdSe nanorods, films of CdSe nanorods and polymer composites with novel charge transfer properties.
Objective 3

Fabricate integrated natural and hybrid self-assembling biomimetic nano-composite materials with efficient broad bandwidth energy capture capabilities
D’Souza et al., Nature Inspired Carbon Nanomaterials for Light Energy Harvesting
Objectives:

- To develop a new protein-based dye-sensitized solar cell based on TiO$_2$ and the extremely stable mycobacterial porin MspA.
- To observe vectorial electron transfer in supramolecular MsPA assemblies on surfaces

Link with other EPSCoR projects:

- Theme II: interface characterization and single nanowire device study (Judy Wu)
- Theme I: new efficient solar cells (Francis D’ Souza), new dyes (Paul Rillema), new solar cell architecture (Jun Li)
Synthesis of MspA-Based Solar Cells

What has been accomplished:

- *M. smegmatis* has been adapted to minimal medium.
- MspA has been isolated and purified in high yields.
- A first prototype for a MspA-based solar cell has been built (in collaboration with Francis D’Souza)

![Diagram of MspA and TiO2](image)
Energy and Charge Transfer in Chlorophyll- and Porphyrin-Based Multichromophore Arrays

Ryszard Jankowiak; Department of Chemistry, KSU
Objective 1

Define basic principles of natural photosynthetic solar energy capture