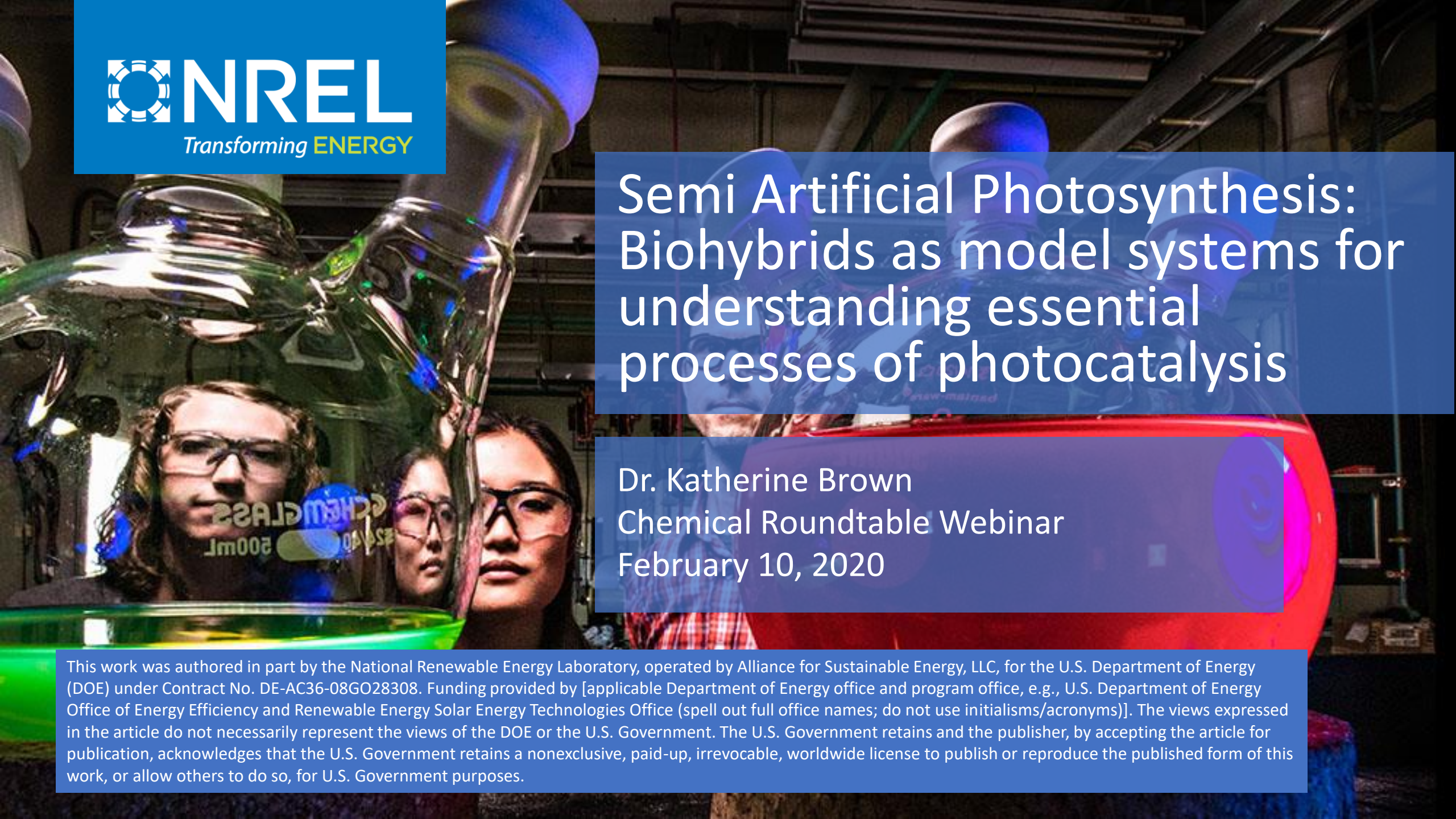


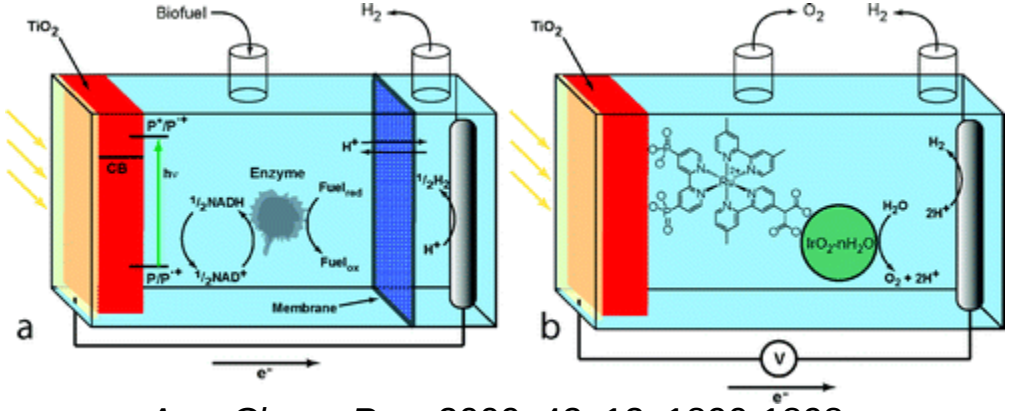
NREL
Transforming ENERGY

# Semi Artificial Photosynthesis: Biohybrids as model systems for understanding essential processes of photocatalysis

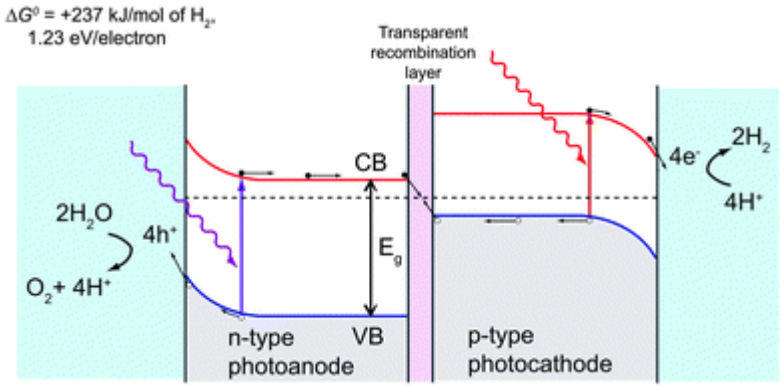
Dr. Katherine Brown
Chemical Roundtable Webinar
February 10, 2020

This work was authored in part by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by [applicable Department of Energy office and program office, e.g., U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Solar Energy Technologies Office (spell out full office names; do not use initialisms/acronyms)]. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

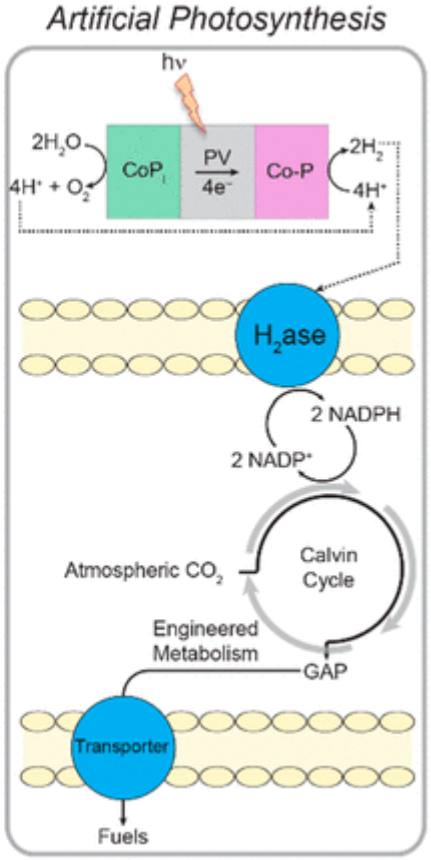
# Artificial Photosynthesis




*Acc. Chem. Res.* 2009, 42, 12, 1890-1898
DOI: 10.1021/ar900209b

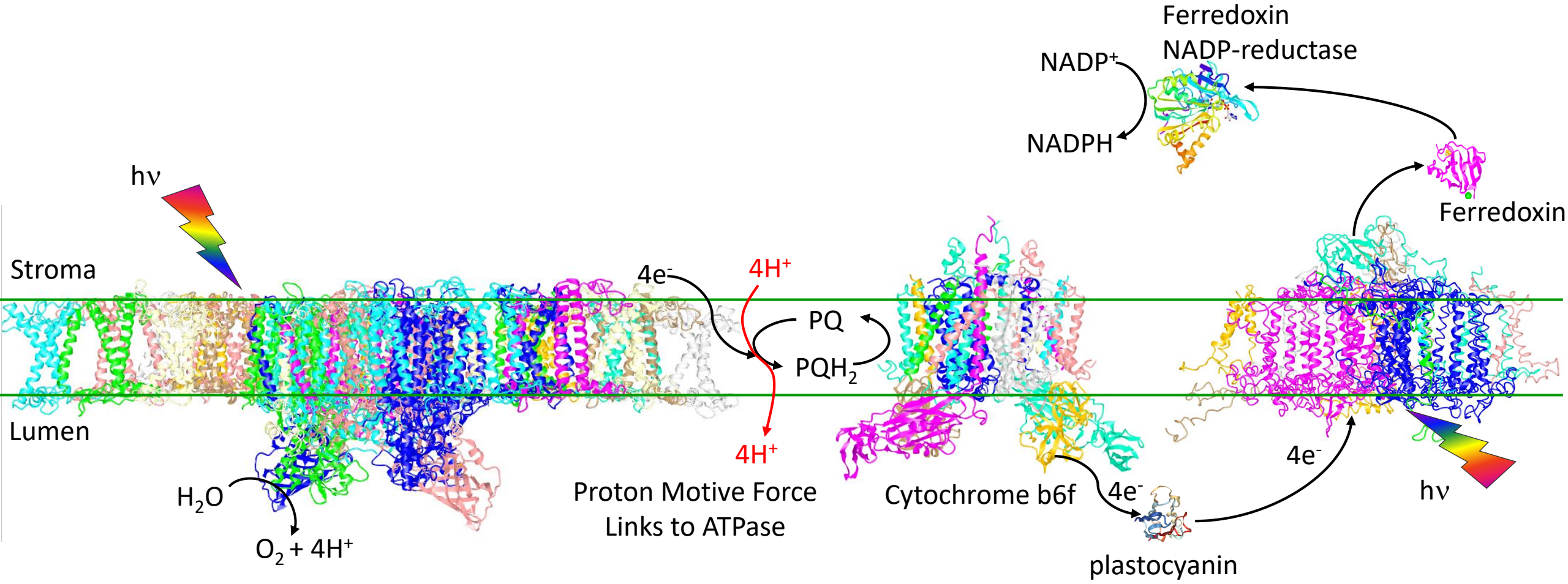



*Energy Environ. Sci.*, 2015, **8**, 2811-2824
DOI: 10.1039/C5EE00457H
Appl. Phys. Lett. 1976 29, 150
DOI: 10.1063/1.89004




*Acc. Chem. Res.* 2019, 52, 11, 3143-3148
DOI: 10.1021/acs.accounts.9b00380

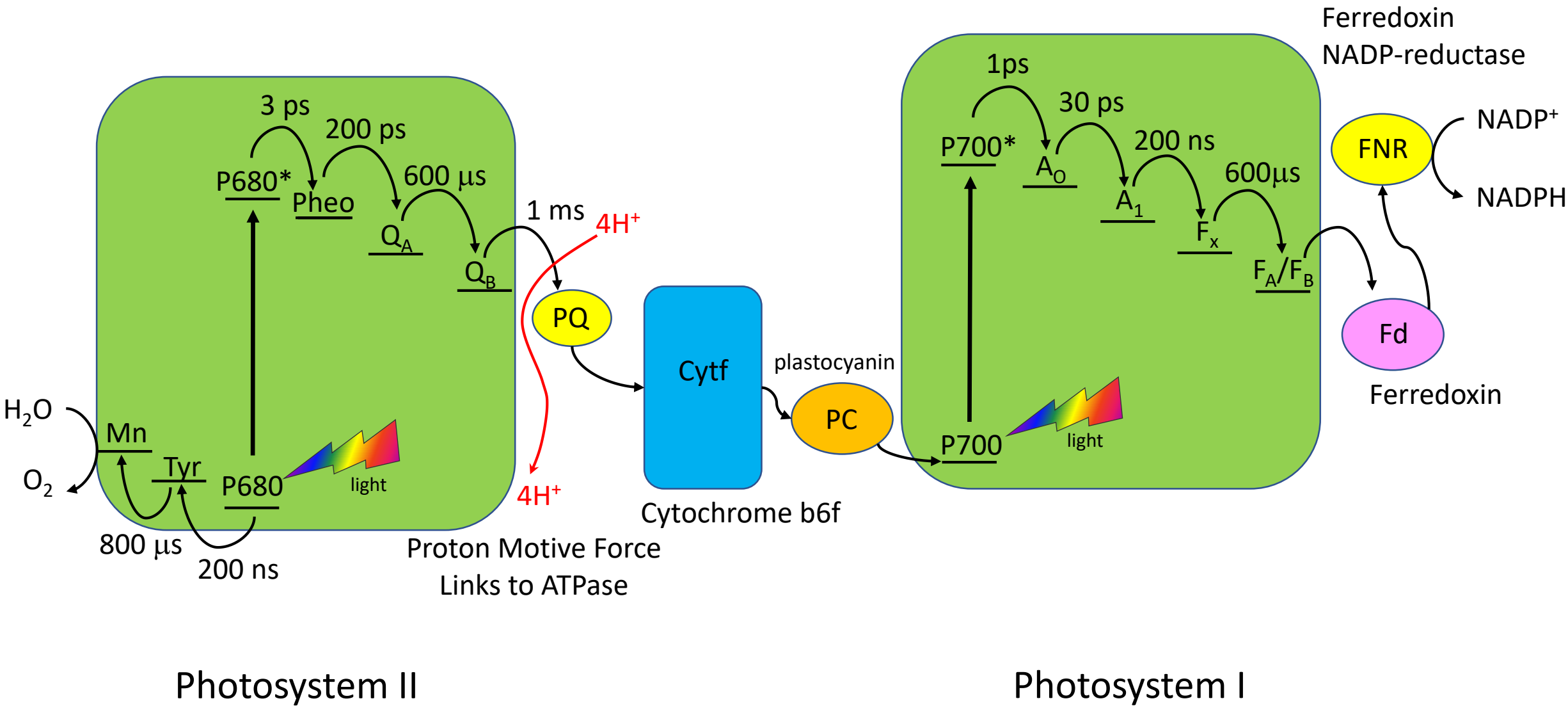
# Natural Photosynthesis



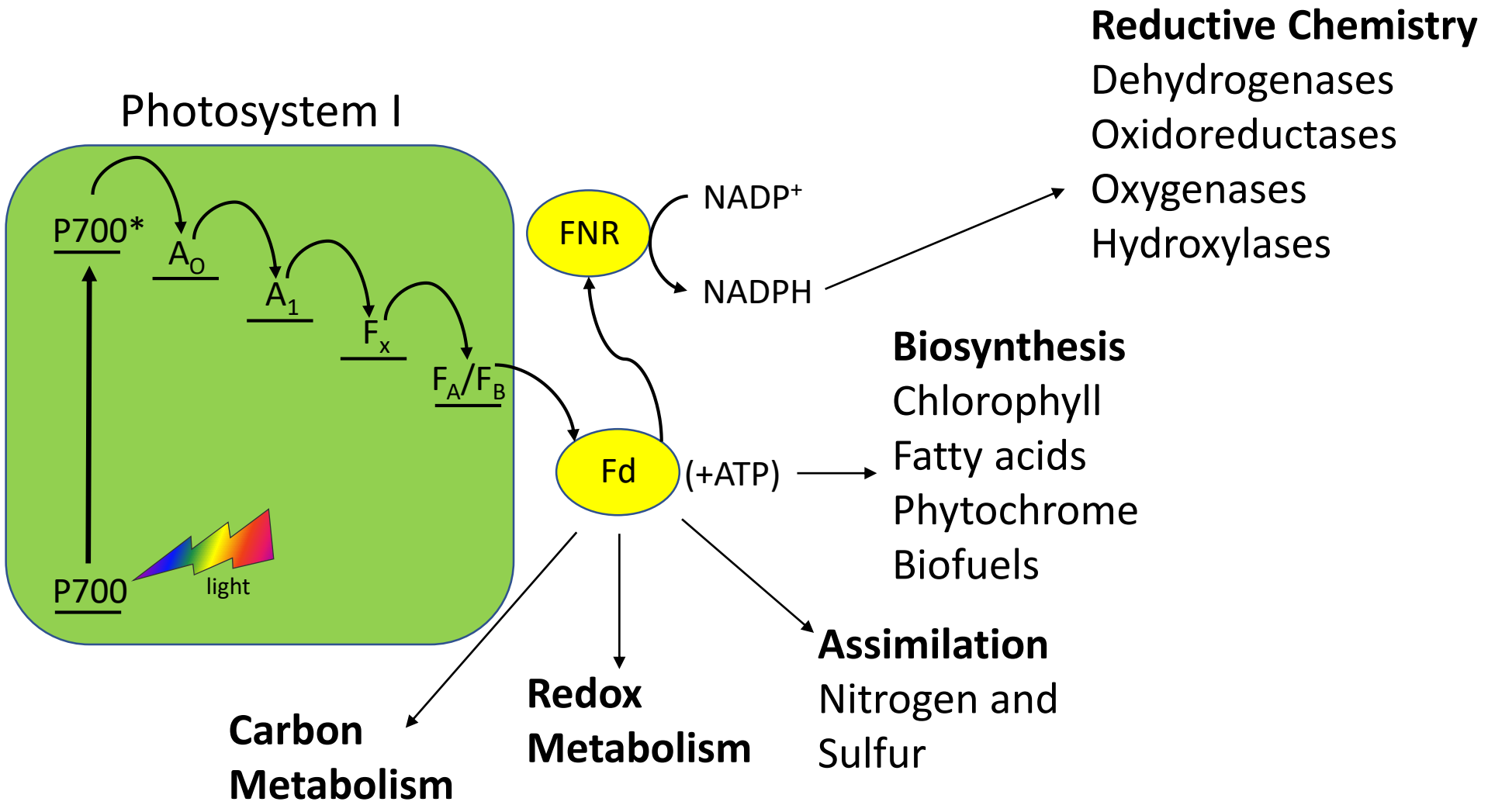

Photosystem II

Photosystem I

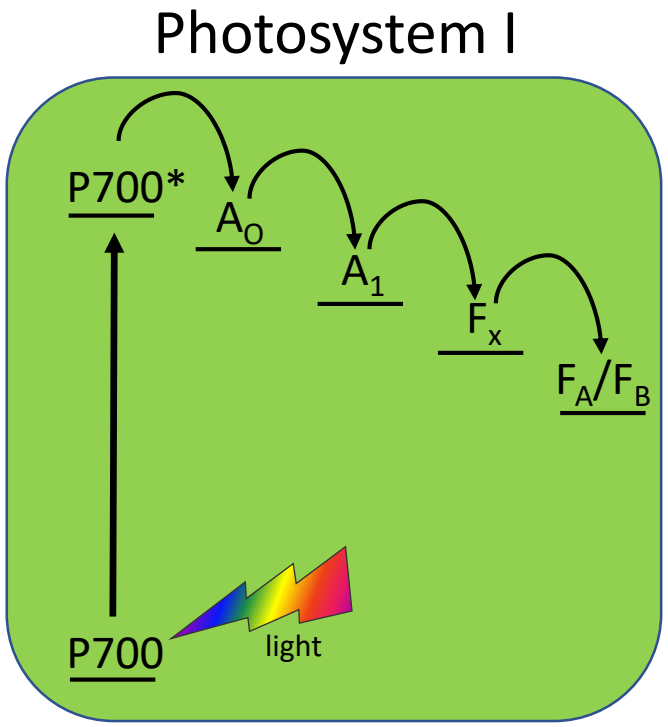
# Natural Photosynthesis

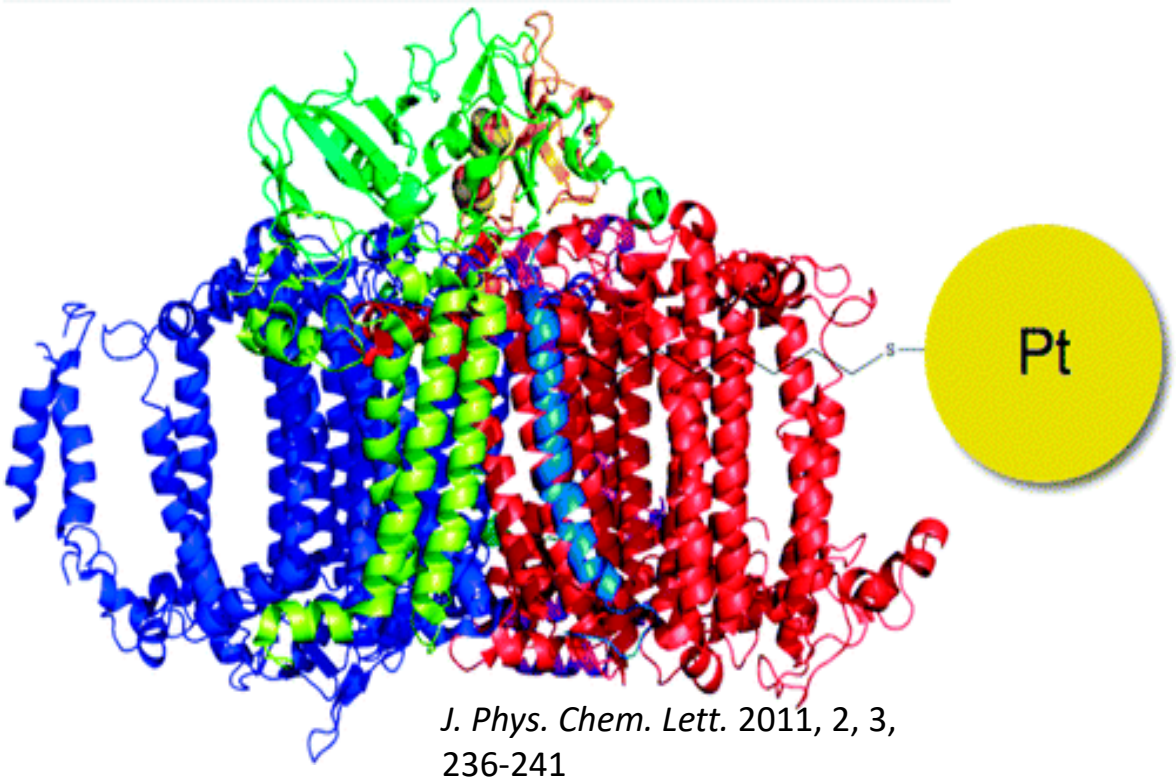


# Photosynthetic Energy Transduction



# Semi-Synthetic Biohybrids
# Photosystem I



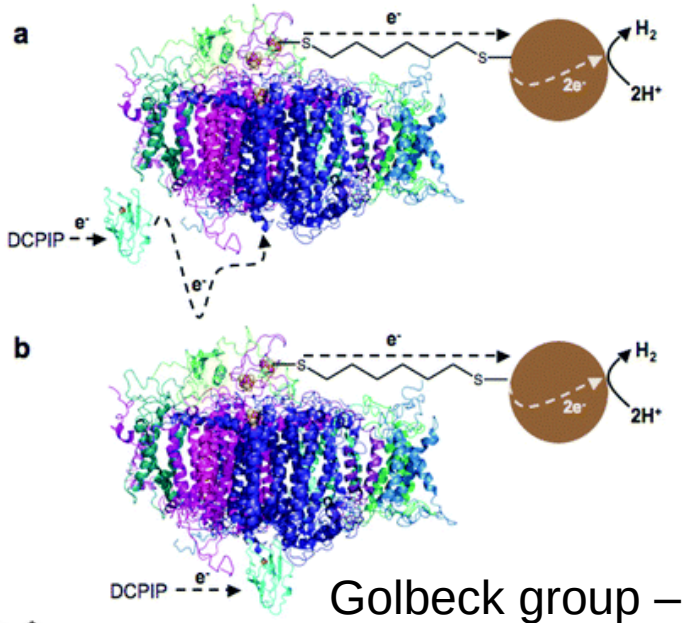



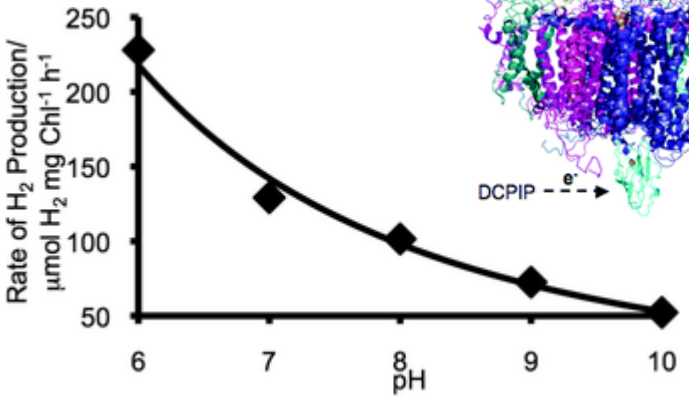

*J. Phys. Chem. Lett.* 2011, 2, 3, 236-241
DOI: 10.1021/jz101728v

# Semi-Synthetic Biohybrids Photosystem I

- PSI can supply light-generated electrons to drive catalysis
- $H^+$ reduction by Pt nanoparticles

**molecular wire/nanoparticle bioconjugates**

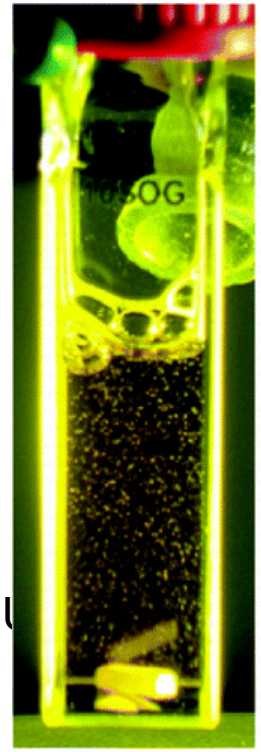


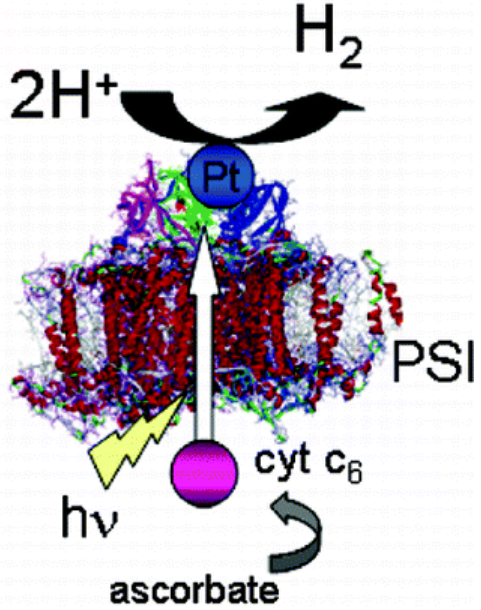




Golbeck group – Penn State U

*Dalton Trans.*, 2009, 10106-10113
DOI: 10.1039/B909137H

**Absorbed nanoparticle bioconjugates**

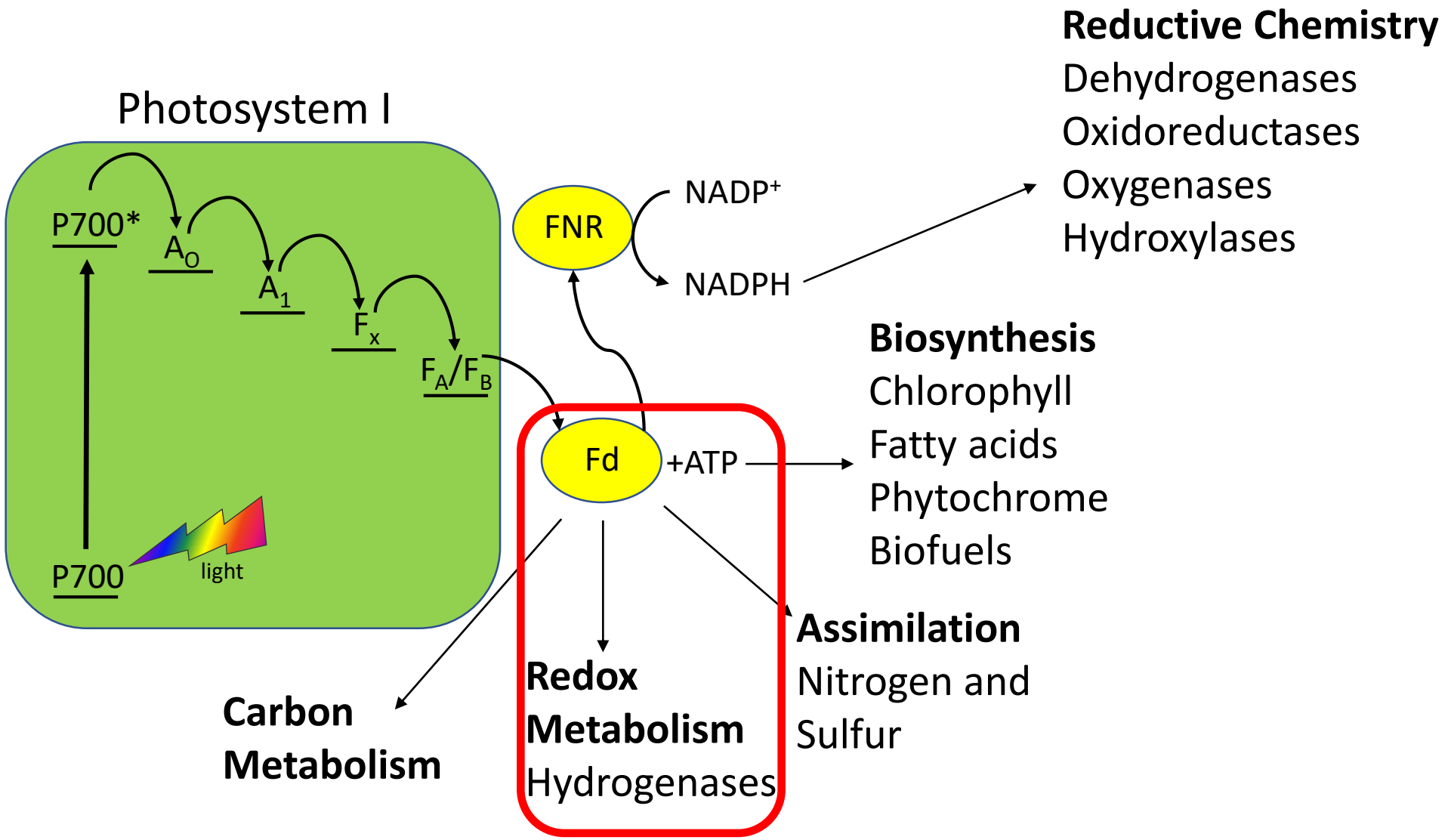


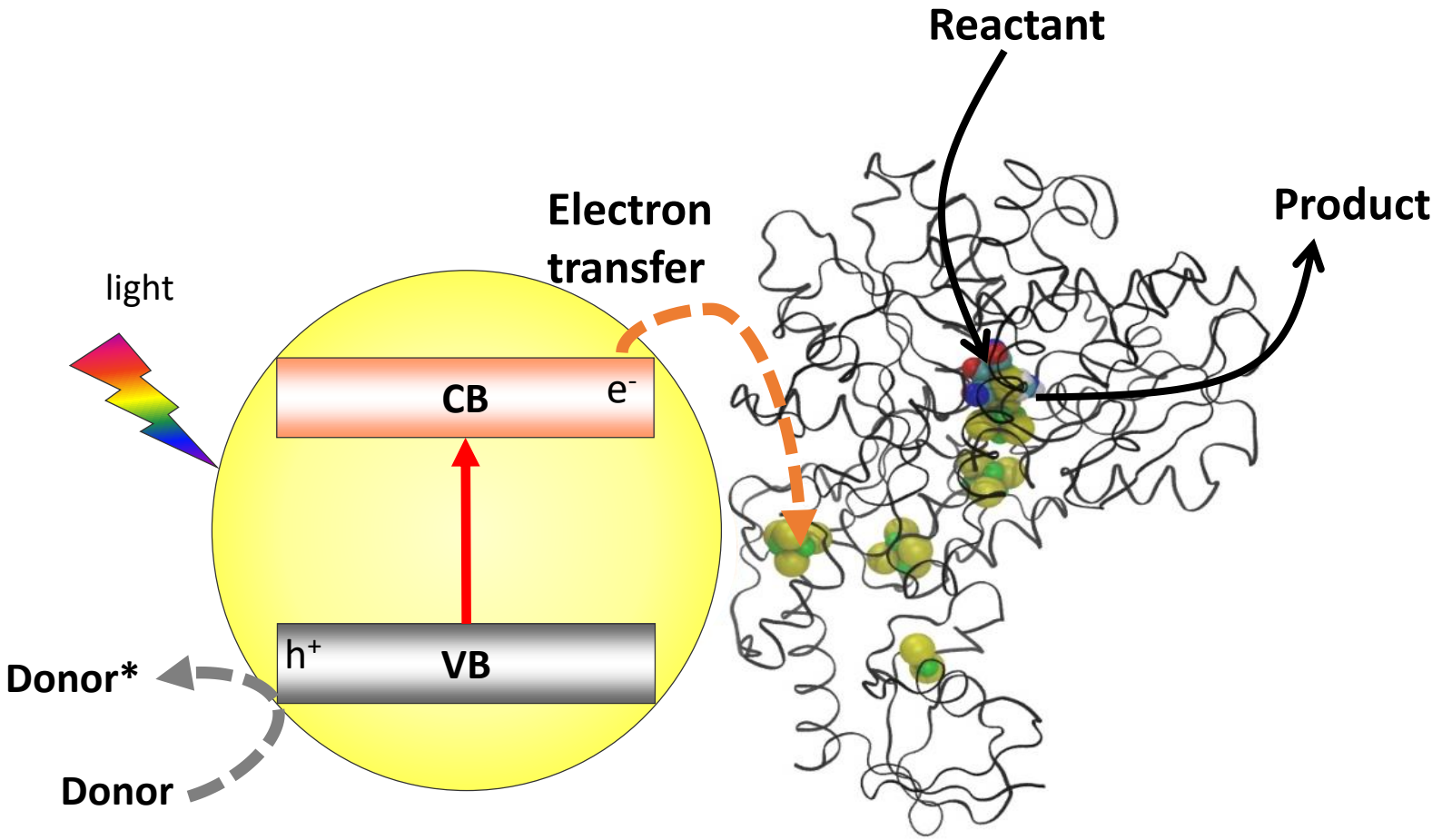

Utschig Group – Argonne National Lab

*J. Phys. Chem. Lett.* 2011, 2, 3, 236-241
DOI: 10.1021/jz101728v

# Photosynthetic Energy Transduction

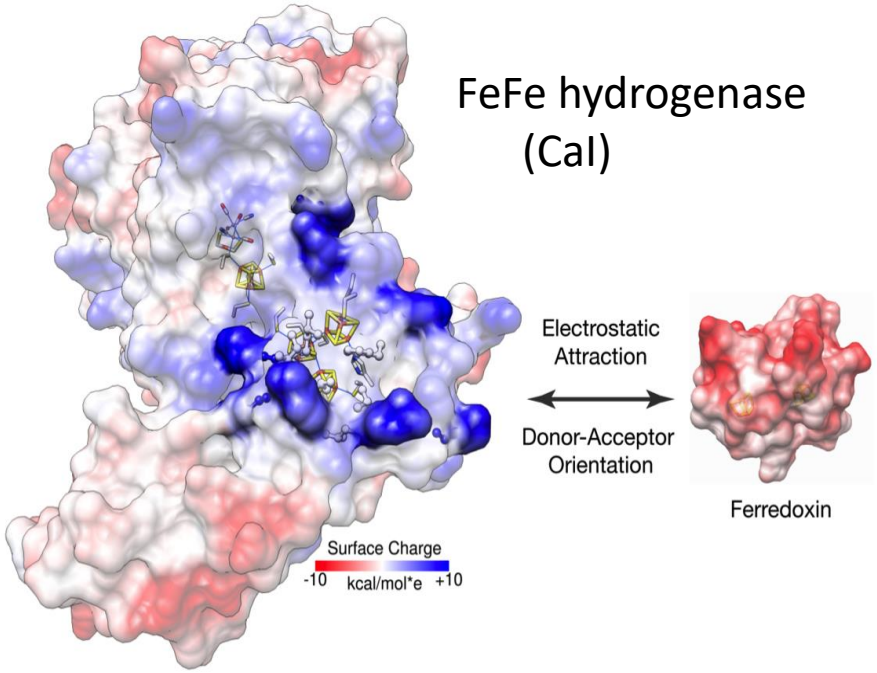


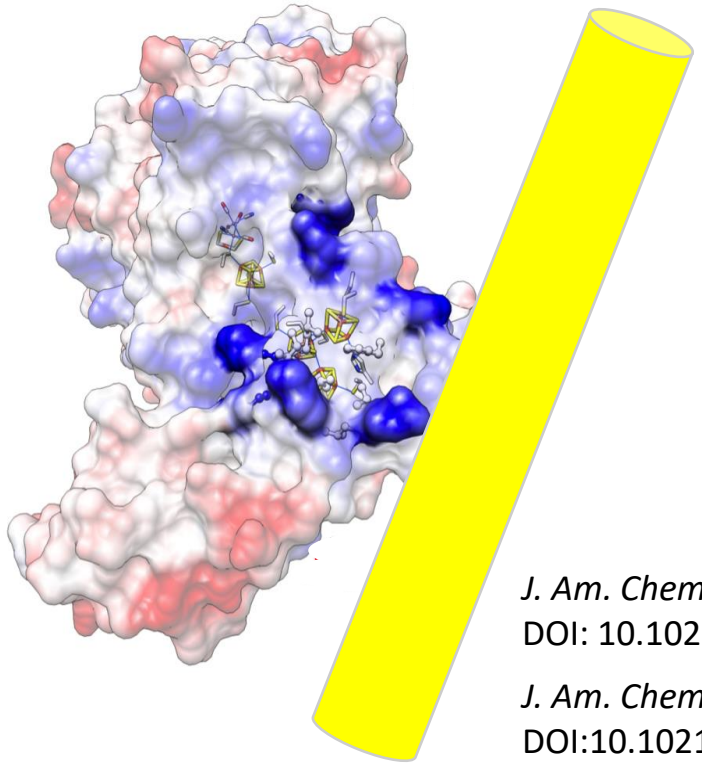
# Semi-Synthetic Biohybrids: Semiconductor Nanoparticle + Enzyme

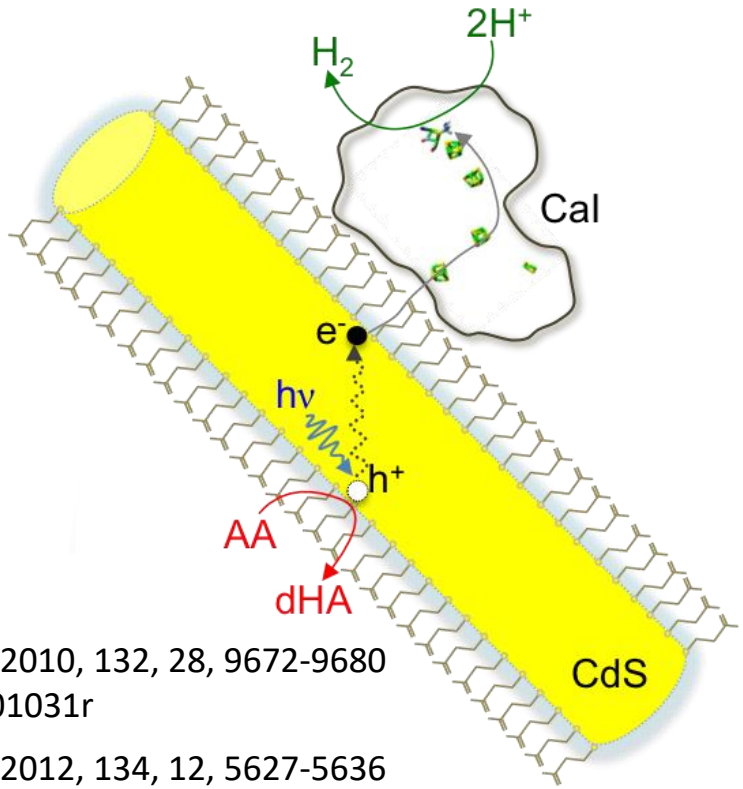



Couple semiconductor nanoparticle light capture and charge generation and seperation to redox enzyme catalysis

# Semi-Synthetic Biohybrids: Semiconductor Nanoparticle + Enzyme





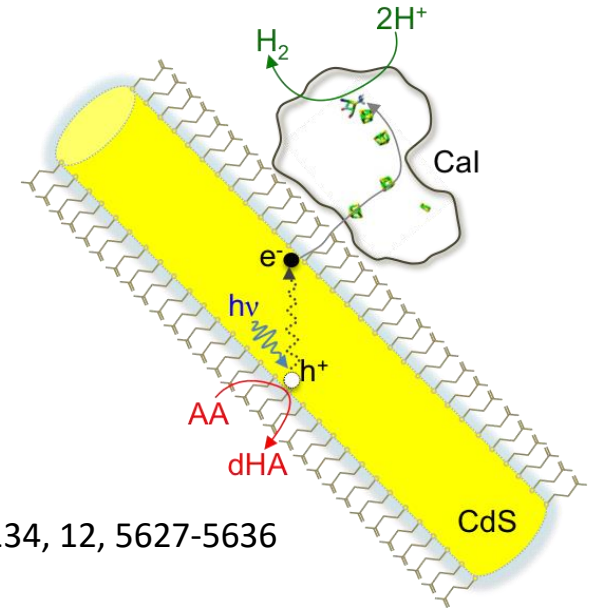

*J. Am. Chem. Soc.* 2010, 132, 28, 9672-9680
DOI: 10.1021/ja101031r

*J. Am. Chem. Soc.* 2012, 134, 12, 5627-5636
DOI:10.1021/ja2116348

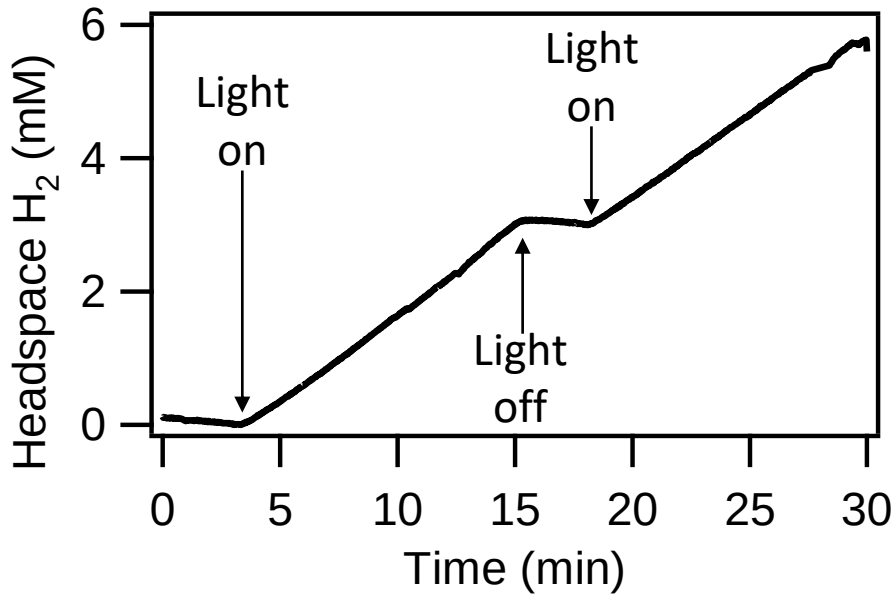
Nanoparticles can mimic biological redox partners (Ferredoxin) to drive enzyme catalysis

- Electrostatic interactions between enzymes and nanoparticle ligand surface

# Nanoparticle-Enzyme Biohybrids: Photocatalysis




*J. Am. Chem. Soc.* 2012, 134, 12, 5627-5636
DOI:10.1021/ja2116348





Gordana Dukovic
U. Colorado

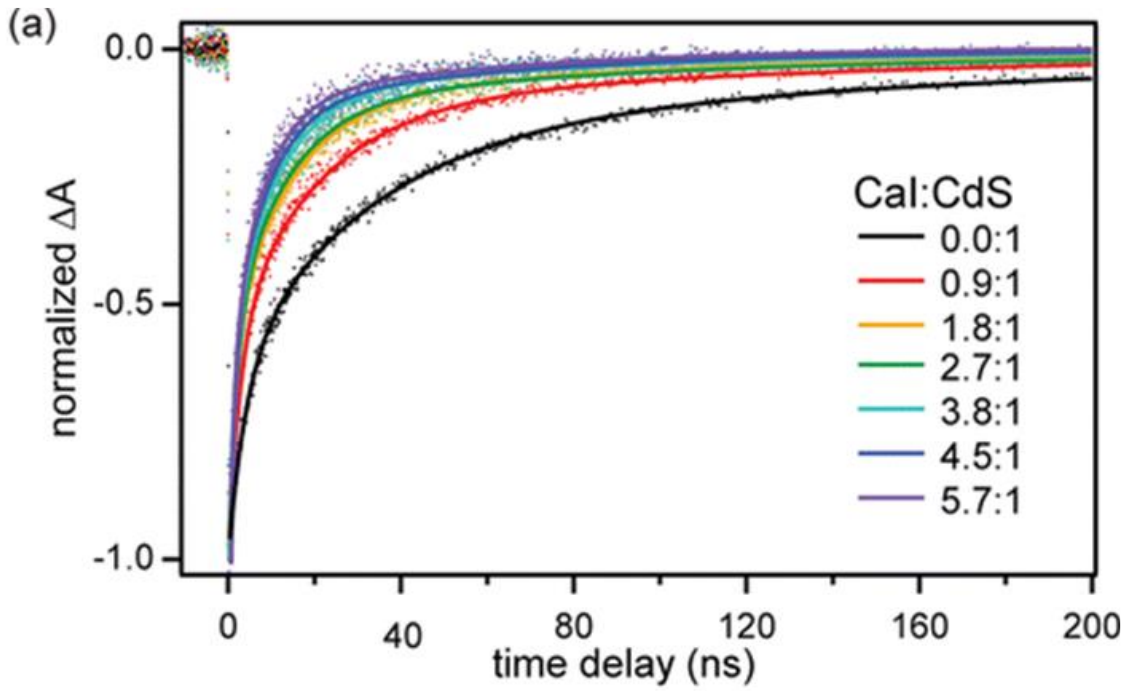

Paul King
NREL

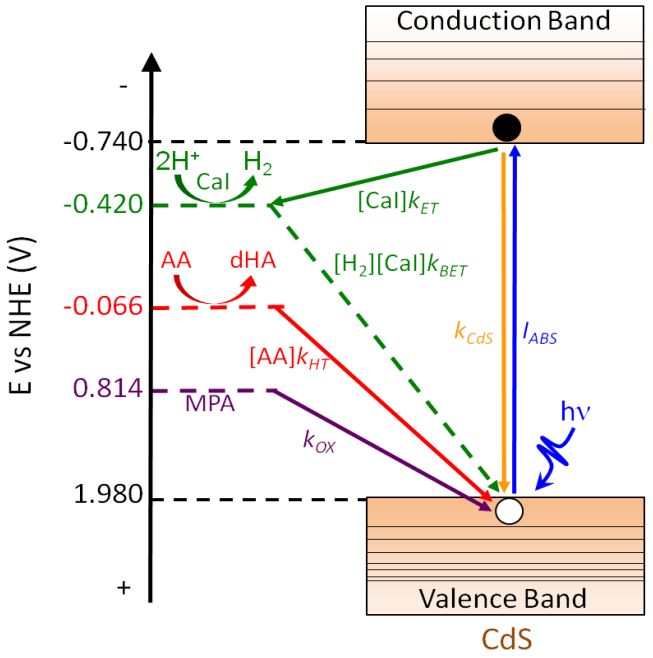

Garry Rumbles
NREL


Molly Wilker
Luther College

Light driven $H_2$ production by hydrogenase biohybrid

# Nanoparticle-Enzyme Biohybrids: Quantifying Electron Transfer Kinetics

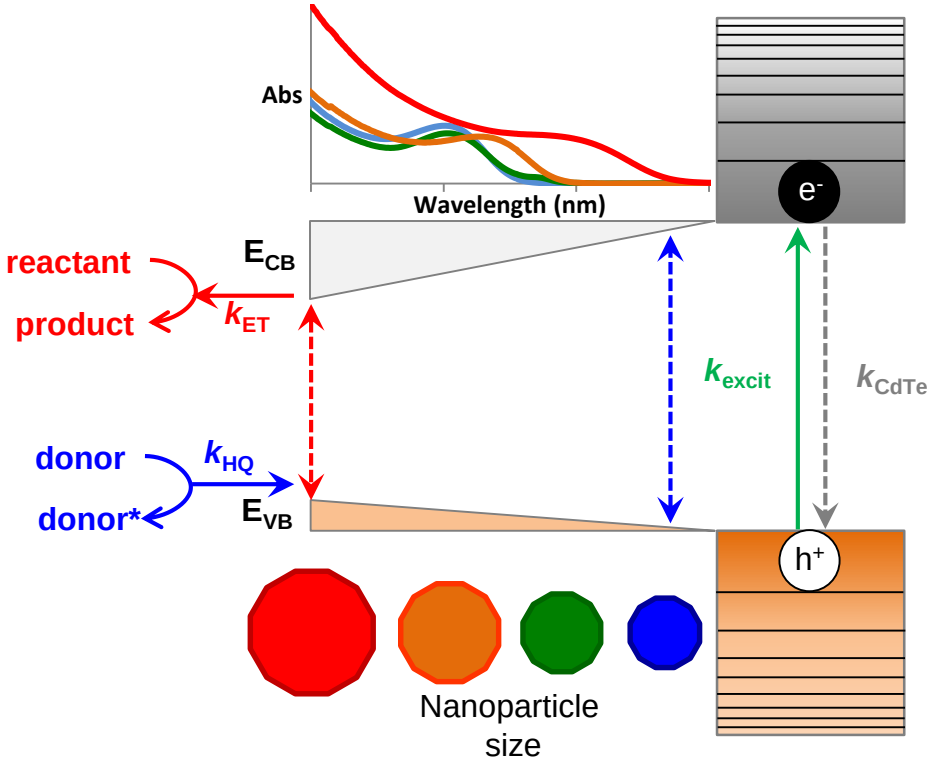


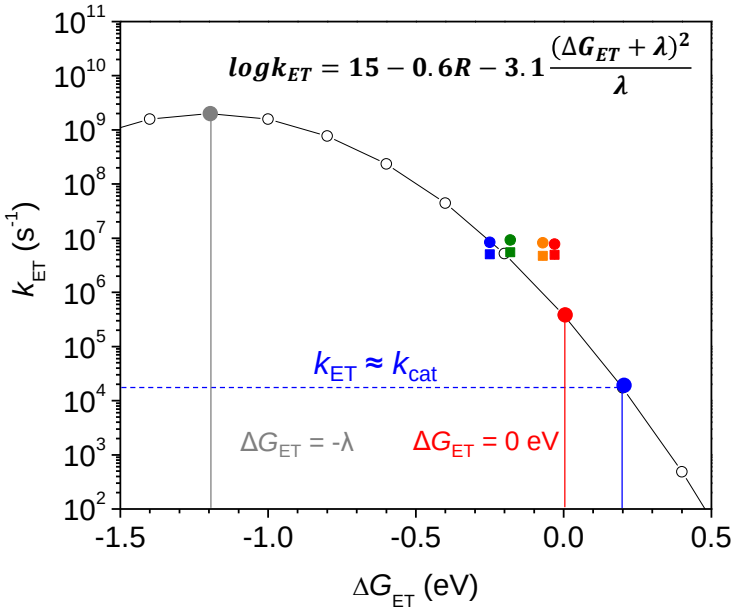




*J. Am. Chem. Soc.* 2014, 136, 11, 4316-4324
DOI: 10.1021/ja413001p

Quantifying electron transfer and quantum efficiency by time-resolved spectroscopy
Overall efficiency of photocatalysis determined by internal processes which must be carefully analyzed and understood

# Nanoparticle-Enzyme Biohybrids: Controlling Electron Potential



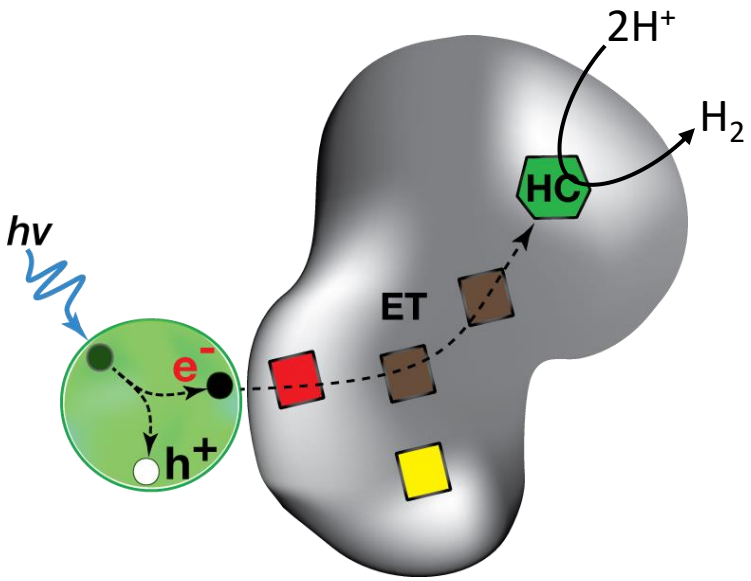

*ACS Nano* 2014, 8, 10, 10790-10798
DOI: 10.1021/nn504561v

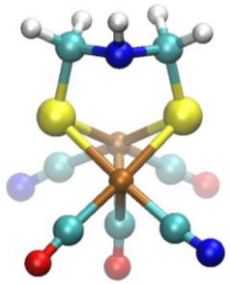
Nanoparticle diameter controls conduction band electron potential

- Quantification of electron transfer rates with varying potential allows study of redox tuning in enzymes
- Elucidates enzyme properties key to their high rates and catalytic efficiency

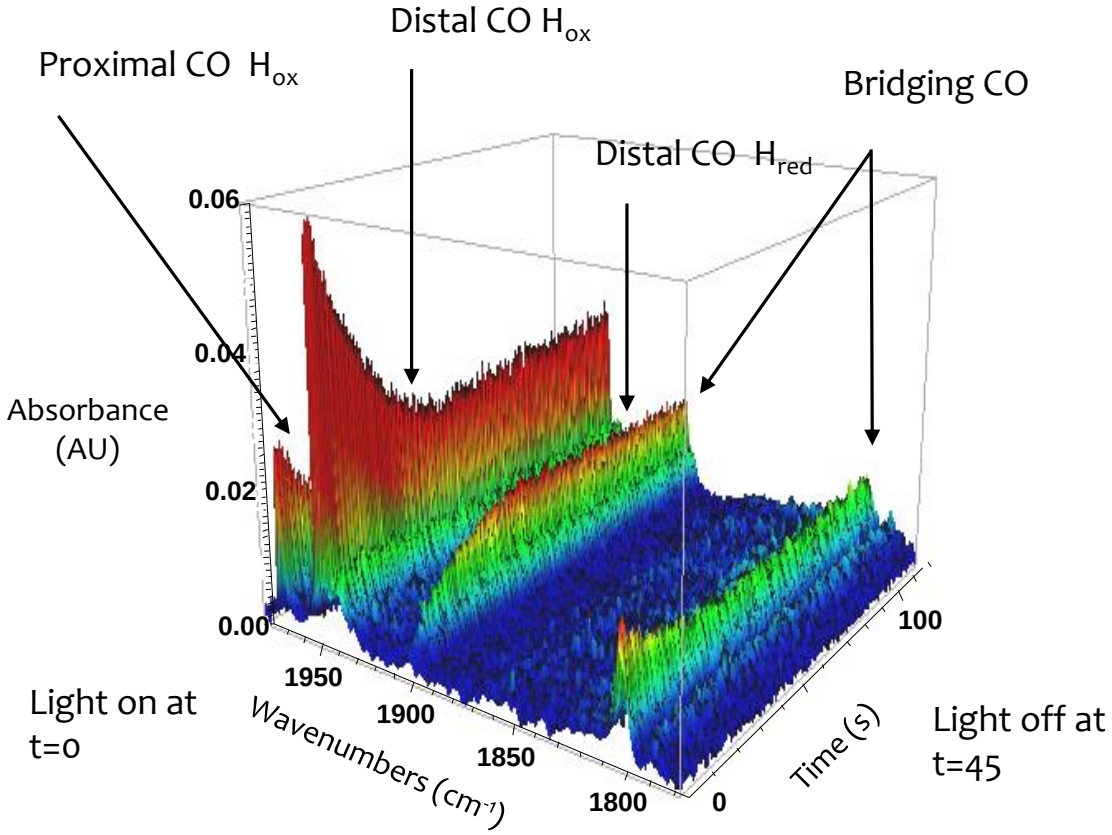
# Nanoparticle-Enzyme Biohybrids: Mechanistic Investigations

*J. Am. Chem. Soc.* 2017, 139, 37, 12879-12882
DOI: 10.1021/jacs.7b04216



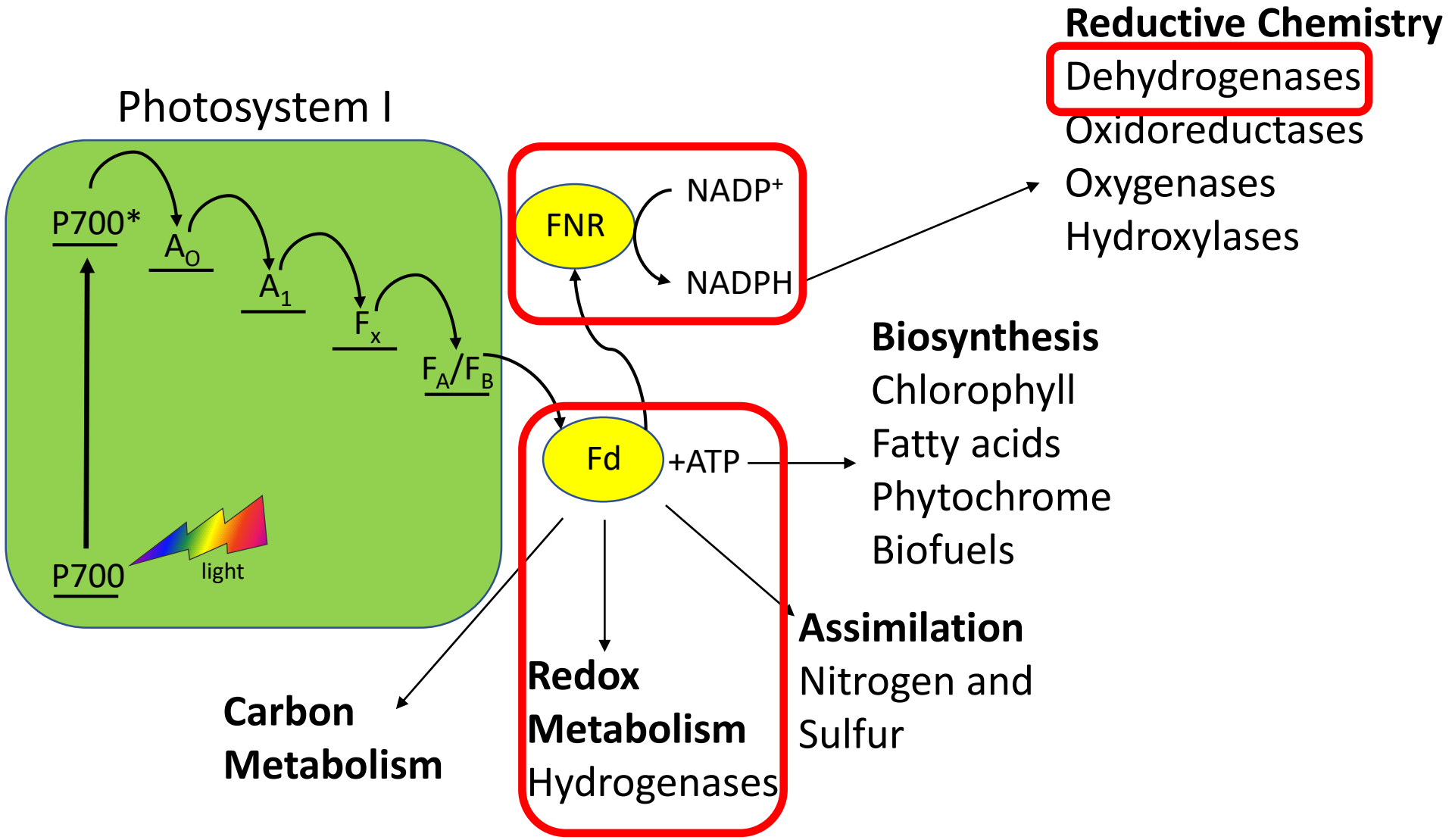
Hydrogenase
Active site structure



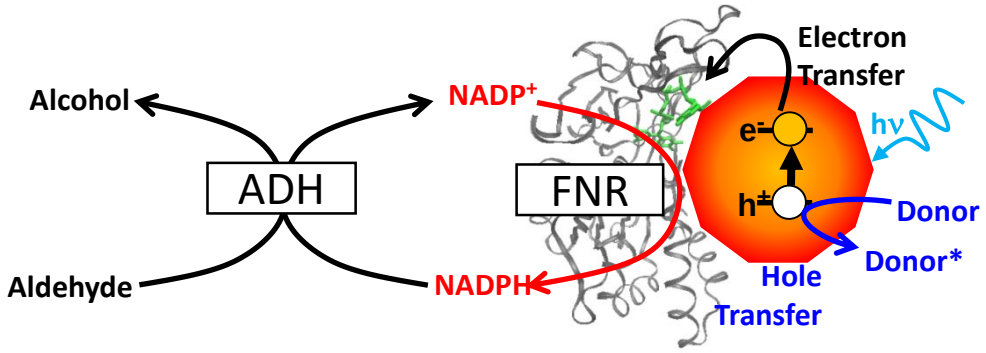

Biohybrid photocatalysis provides an opportunity to study catalytic turnover in novel ways

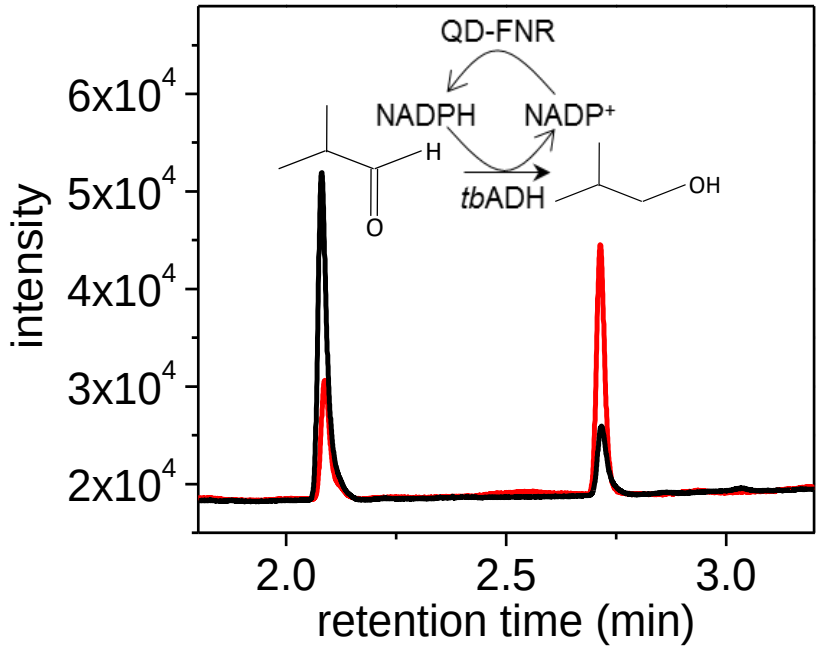
- Time-resolved spectroscopy of active site changes
- Temperature controlled catalysis – electron transfer conditions not available in biology

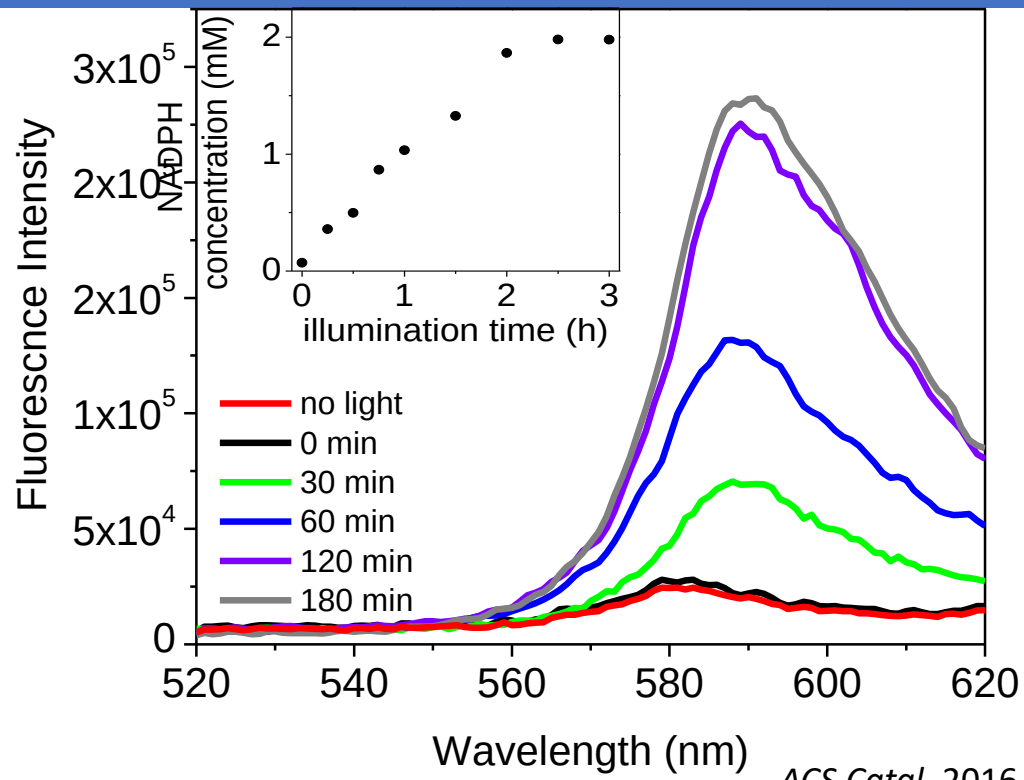
# Photosynthetic Energy Transduction



# Nanoparticle-Enzyme Biohybrids: Cofactor Regeneration




*ACS Catal.* 2016, 6, 4, 2201-2204
DOI: 10.1021/acscatal.5b02850

Ferredoxin NADP-reductase biohybrids photocatalyze regeneration of NADPH

- Coupled to alcohol dehydrogenase to produce biofuels

# Nanoparticle-Enzyme Biohybrids: Nitrogen Reduction

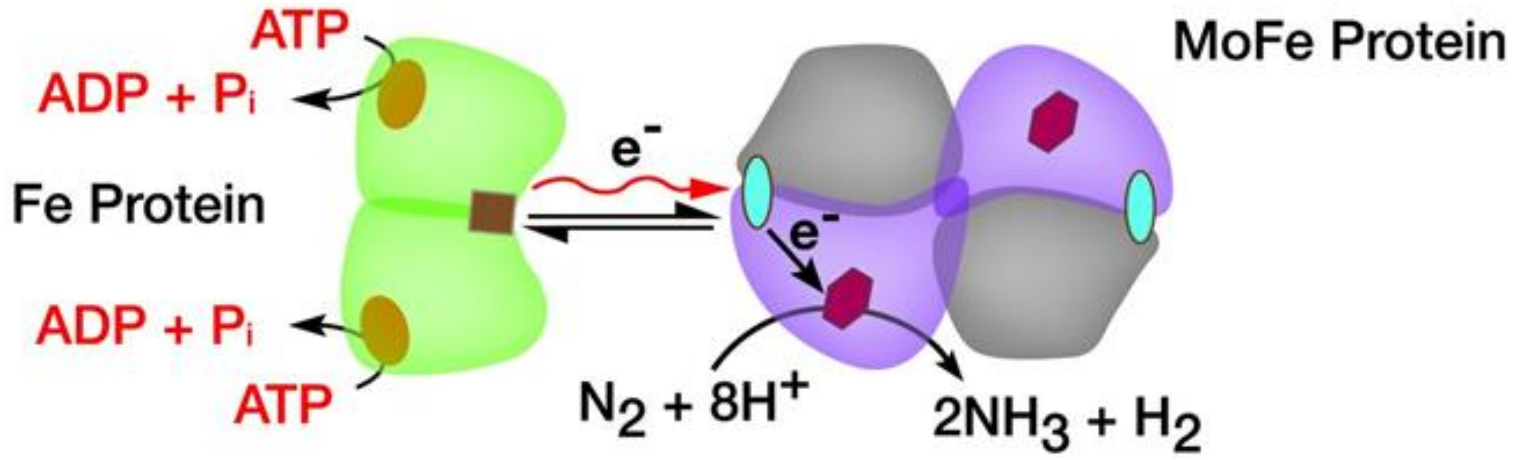
Industrial $N_2$ fixation (Haber-Bosch Process)

- High temperature and pressure
- Fossil fuel intensive (up to 1% of global energy use)

Biological $N_2$ fixation

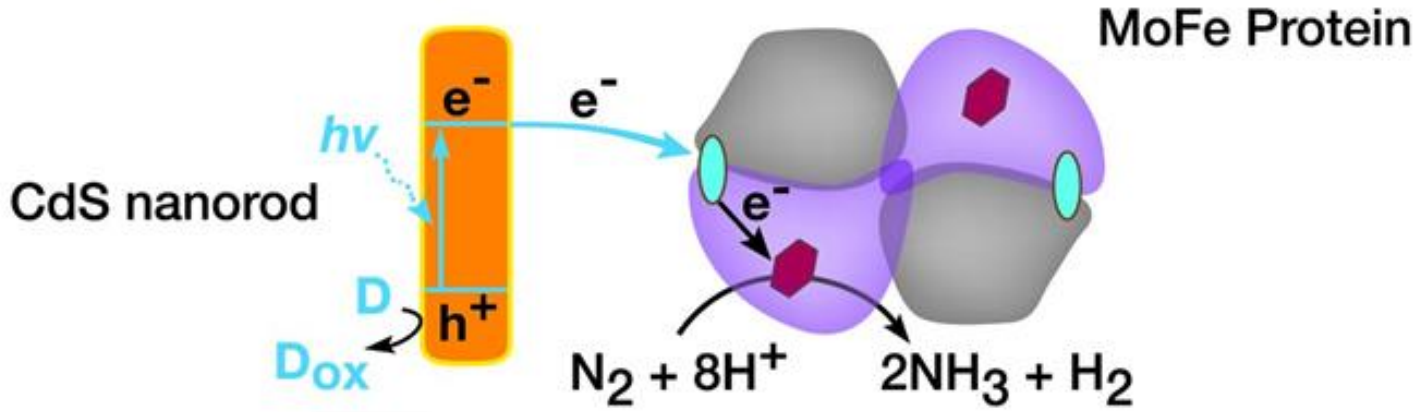
- Ambient conditions
- High biological energy demand

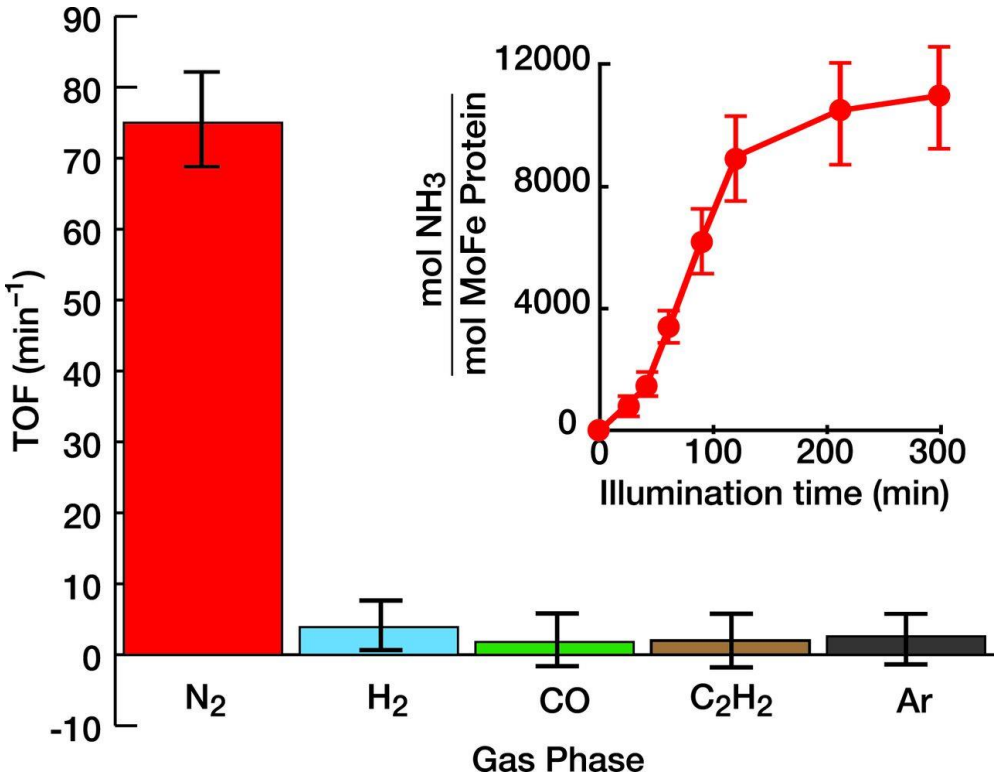
$$N_2 + 8H^+ + 8e^- + 16ATP \rightarrow 2NH_3 + H_2 + 16ADP/P_i$$



# Nanoparticle-Enzyme Biohybrids: Nitrogen Reduction

$$N_2 + 8H^+ + 8e^- + nhv \rightarrow 2NH_3 + H_2$$




Lance Seefeldt
Utah State U.

John Peters
Washington State U.

*Science* 2016, 352, 6284, 448-450
DOI: 10.1126/science.aaf2091

Gordana Dukovic
U. Colorado

Paul King
NREL

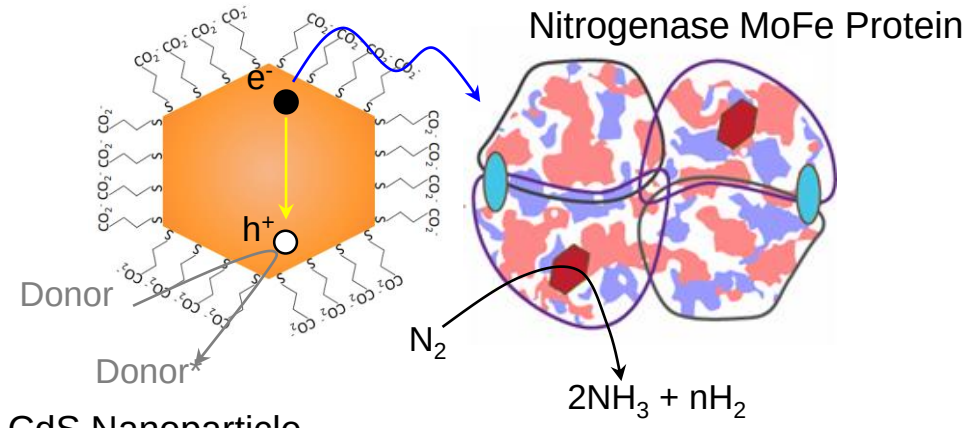
Nanoparticle can replace biological electron donor and circumvent ATP requirement for $N_2$ reduction

- Photocatalytic $NH_3$ production ~70% biological maximum
- $NH_3$ production inhibited by known enzyme inhibitors

# Nanoparticle-Enzyme Biohybrids: Mechanistic Investigations of Nitrogenase

## Product Selectivity

- $H_2$ is a co-product of $NH_3$
- $H_2/NH_3$ ratio changes with reaction conditions

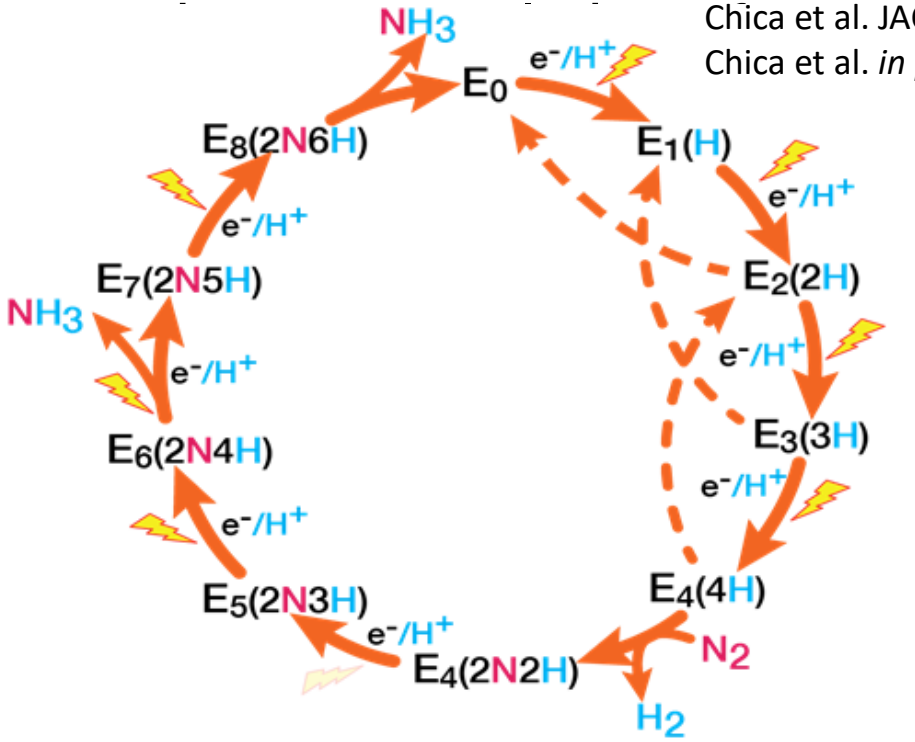



Brown et al. *in preparation*

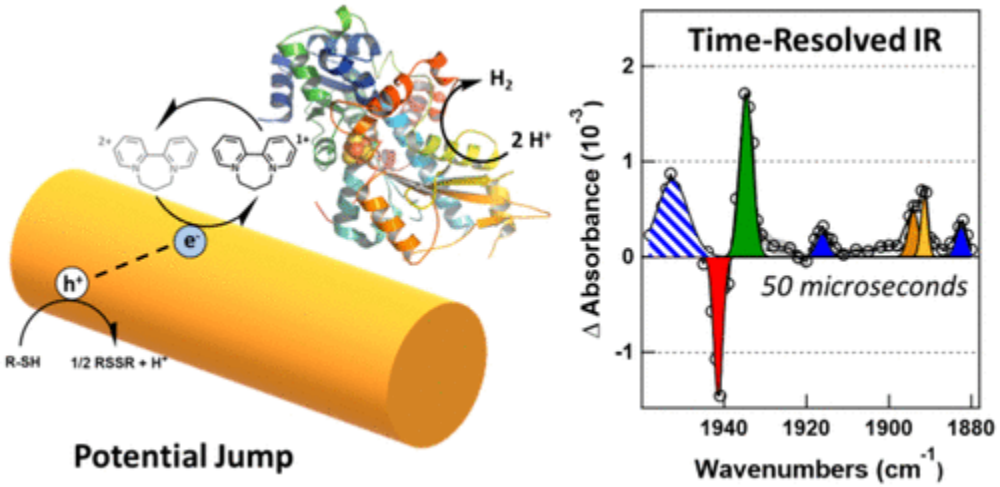
## Reaction Mechanism

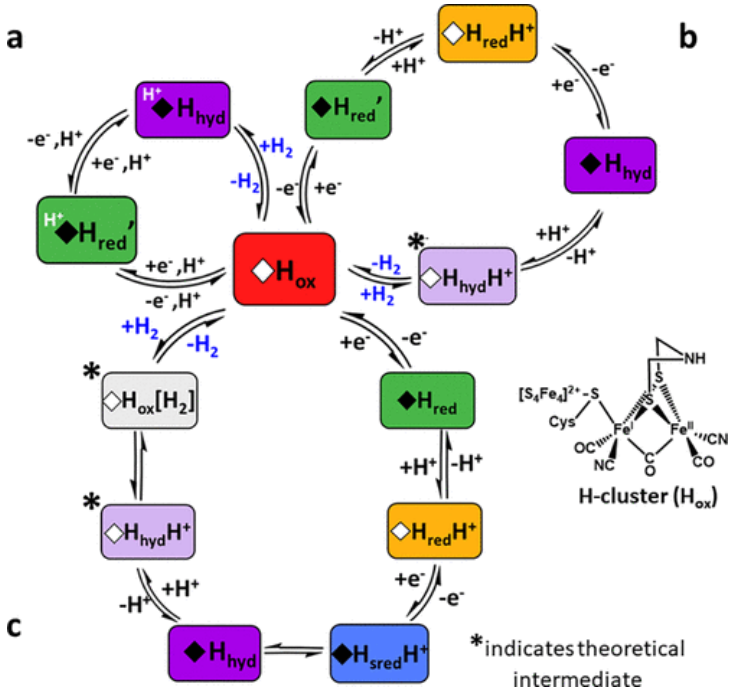
- Sequential electron transfer steps
- $N_2$ binding and reduction

Chica et al. JACS (*in Review*)
Chica et al. *in preparation*



# Semi-Synthetic Biohybrids: Nanomaterial-Enzyme Biohybrids



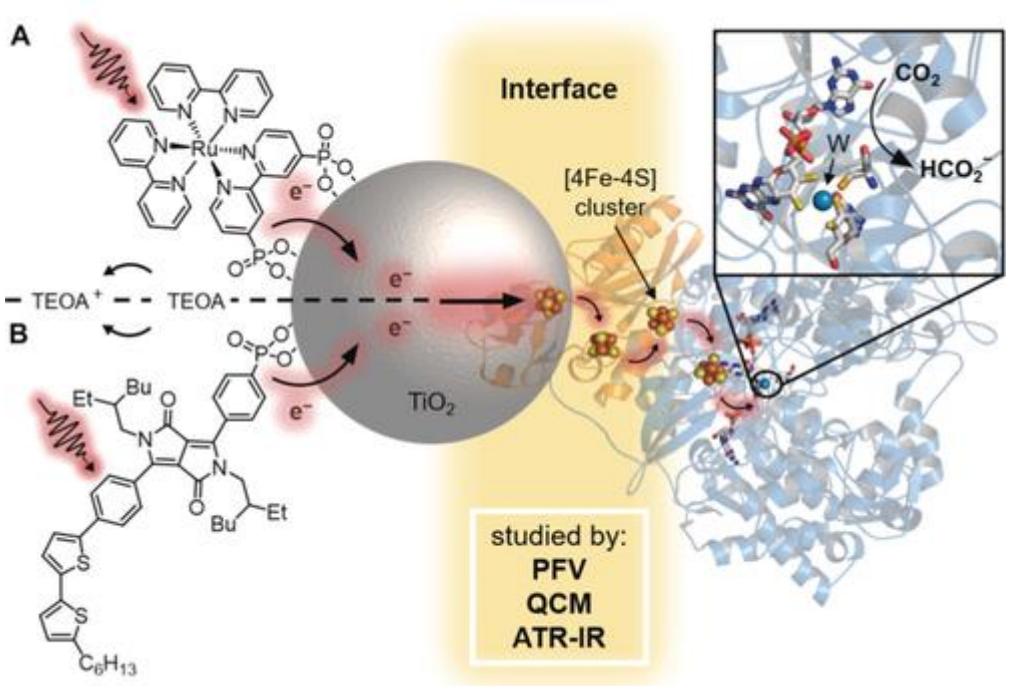

Dyer Group – Emory University

*J. Am. Chem. Soc.* 2019, 141, 40, 16064-16070
DOI: 10.1021/jacs.9b08348

Time-Resolved mechanistic studies of hydrogenase active sites

# Semi-Synthetic Biohybrids: Nanomaterial-Enzyme Biohybrids

## $CO_2$ reduction to formate

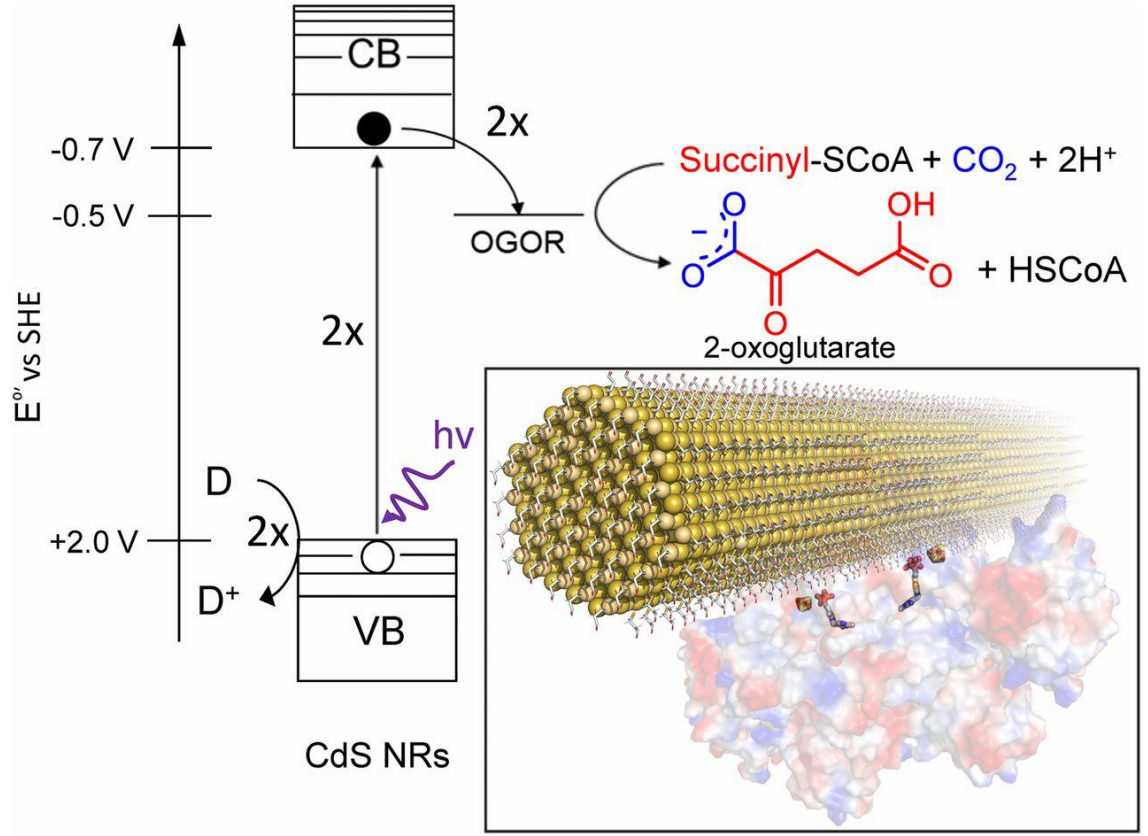



Reisner Group – Cambridge University

Angewandte Chemie. 2019, 131, 14, 4649-4653

DOI: 10.1002/ange.201814419

## Carbon-Carbon bond formation by $CO_2$ reduction



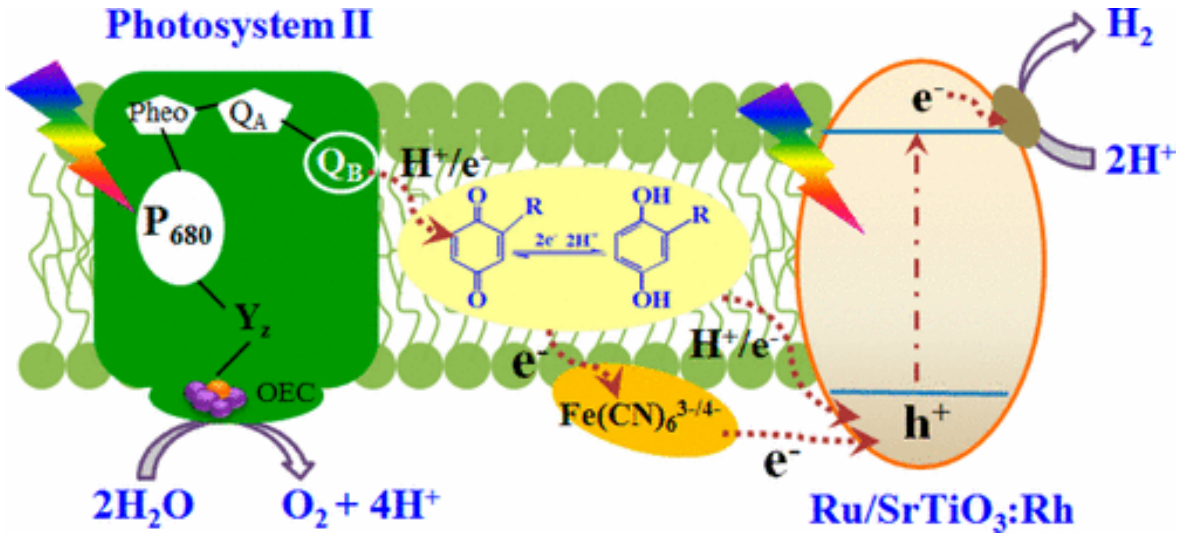

Dukovic Group – University of Colorado

*PNAS* 2020 117 (1) 135-140

DOI: 10.1073/pnas.1903948116

# Semi-Synthetic Biohybrids: Photosystem II based Biohybrids

Linking Photosystem II water oxidation to nanoparticle catalysis

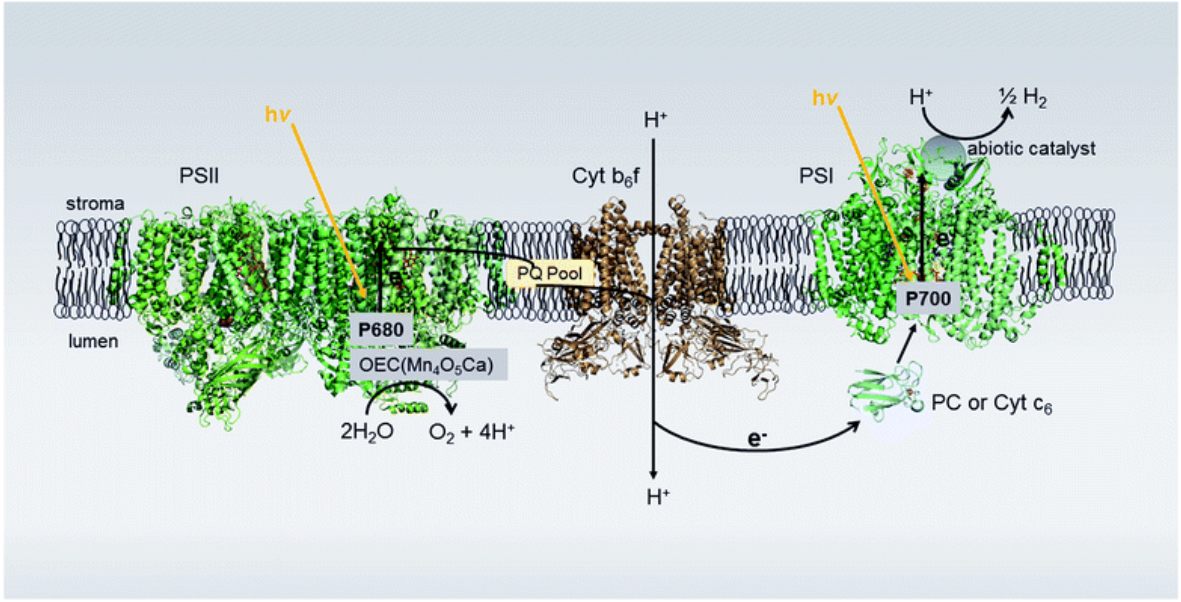



Li Group - Dalian National Laboratory for Clean Energy

*J. Phys. Chem. C* 2017, 121, 5, 2605-2612

DOI: 10.1021/acs.jpcc.6b12002

Semi synthetic systems with nanoparticles replacing PSI




Utschig Group – Argonne National Laboratory

*Chem. Sci.*, 2018, **9**, 8504-8512

DOI: 10.1039/C8SC02841A

Full thylakoid membranes with nanoparticles replacing Ferredoxin

# Acknowledgements

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Cara Lubner
Mike Ratzloff
Bryant Chica

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**Washington State University:** John W. Peters
**Carnegie-Mellon University:** Ruixi Fan, Yisong (Alex) Guo,
**NREL:** Garry Rumbles, Justin Johnson, Nate Neale, Andrew Ferguson, John Turner

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NREL Laboratory Directed Research and Development (LDRD) Program

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