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## Catalytic solar water splitting inspired by photosynthesis. homogeneous catalysts with a Mechanical ("Machine-like") action

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## Catalytic solar water splitting inspired by photosynthesis. homogeneous catalysts with a Mechanical ("Machine-like") action

### Abstract

Chemical reactions may be controlled by either: the minimum threshold energy that must be overcome during collisions between reactant molecules / atoms (the Activation Energy,  $E_a$ ), or: the rate at which reactant collisions occur (the Collision Frequency,  $A$ ) (for reactions with low  $E_a$ ). Reactions of type (2) are governed by the physical, mechanical interaction of the reactants. Such mechanical processes are unusual, but not unknown in molecular catalysts. We examine the catalytic action and macroscopic properties of several abiological mechanical catalysts and show that they display distinct similarities to enzymes in general. An abiological model of the Photosystem II Water Oxidizing Complex that appears to employ a mechanical action has now been found to be a remarkably active and sustained molecular catalyst of water oxidation when illuminated by sunlight. A free-standing Dye-Sensitized Solar Cell that spontaneously splits water into hydrogen and oxygen has been developed using this catalyst.

### Keywords

mechanical, machine, like, homogeneous, action, photosynthesis, inspired, splitting, water, solar, catalytic, catalysts

### Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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# Catalytic Solar Water Splitting Inspired by Photosynthesis. Homogeneous Catalysts with a Mechanical (“Machine-Like”) Action

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**INTELLIGENT POLYMER**  
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## *Sub-theme: Molecular Machines*

- Much interest in developing "*molecular machines*" that drive chemical reactions
- But, what is the "*mechanical action*" that must occur within a molecular catalyst to turn it into a *molecular machine*?

# Two General Methods of Inducing Change

- **Energy Gradient (" *Thermodynamics* ")**

Change driven by an overall release of energy

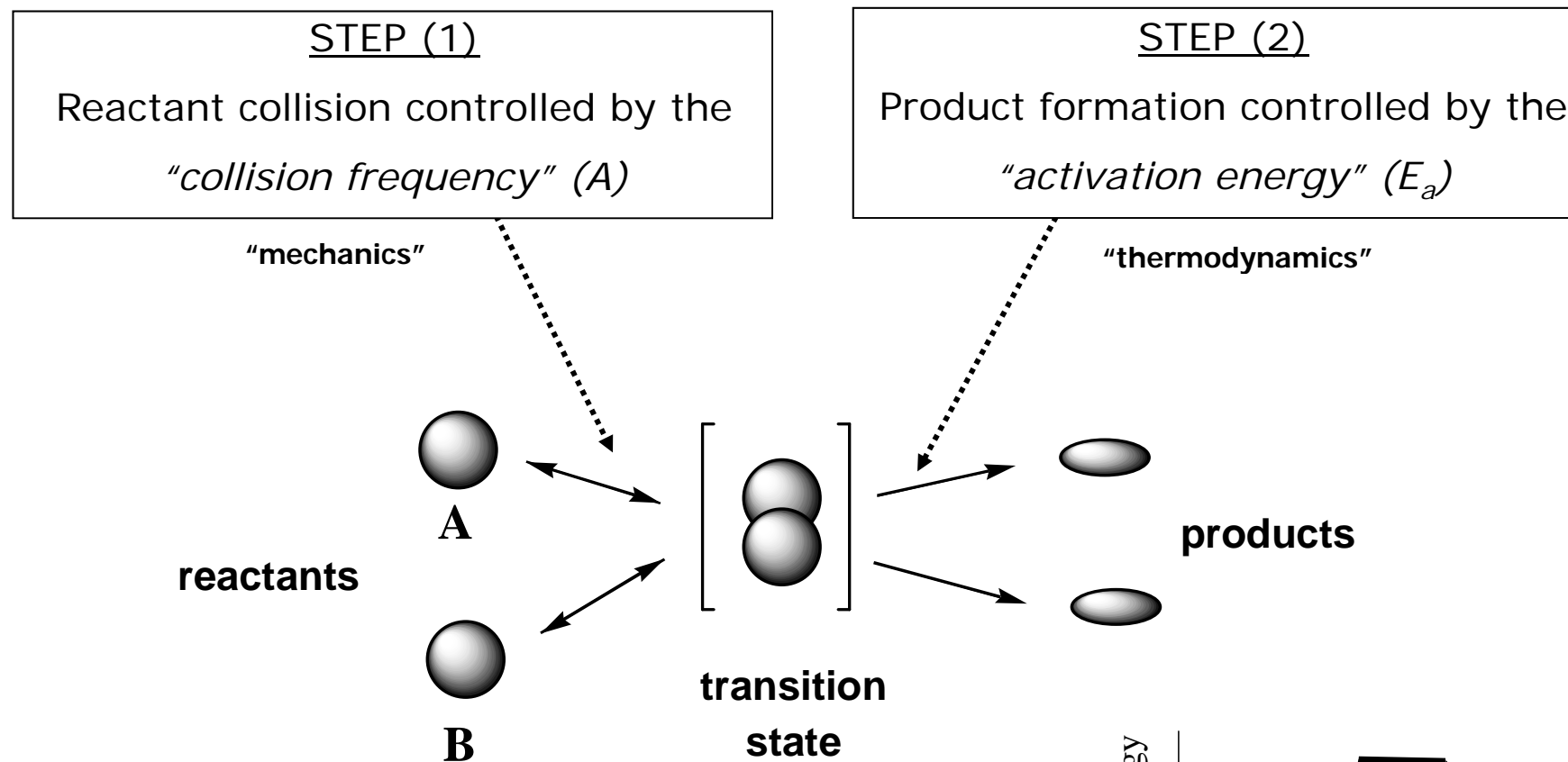
e.g. a ball falling to Earth under gravity

- **Mechanical Interaction (" *Mechanics* ")**

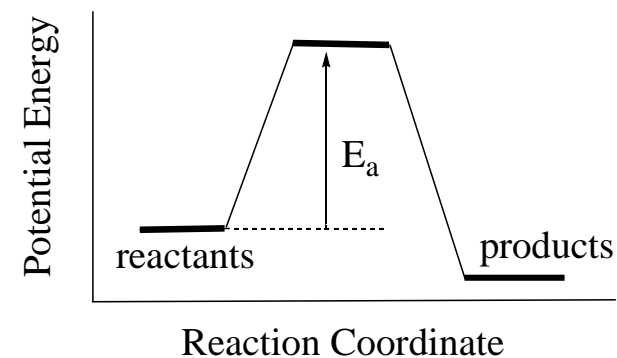
Change driven by a physical collision (action-reaction sequence that plays out over time)

e.g. two billiard balls physically colliding

# Chemistry: Collision Theory



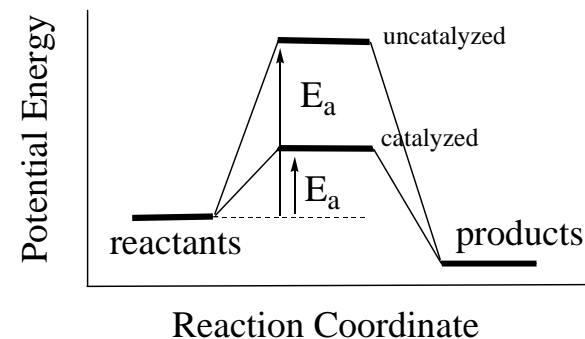
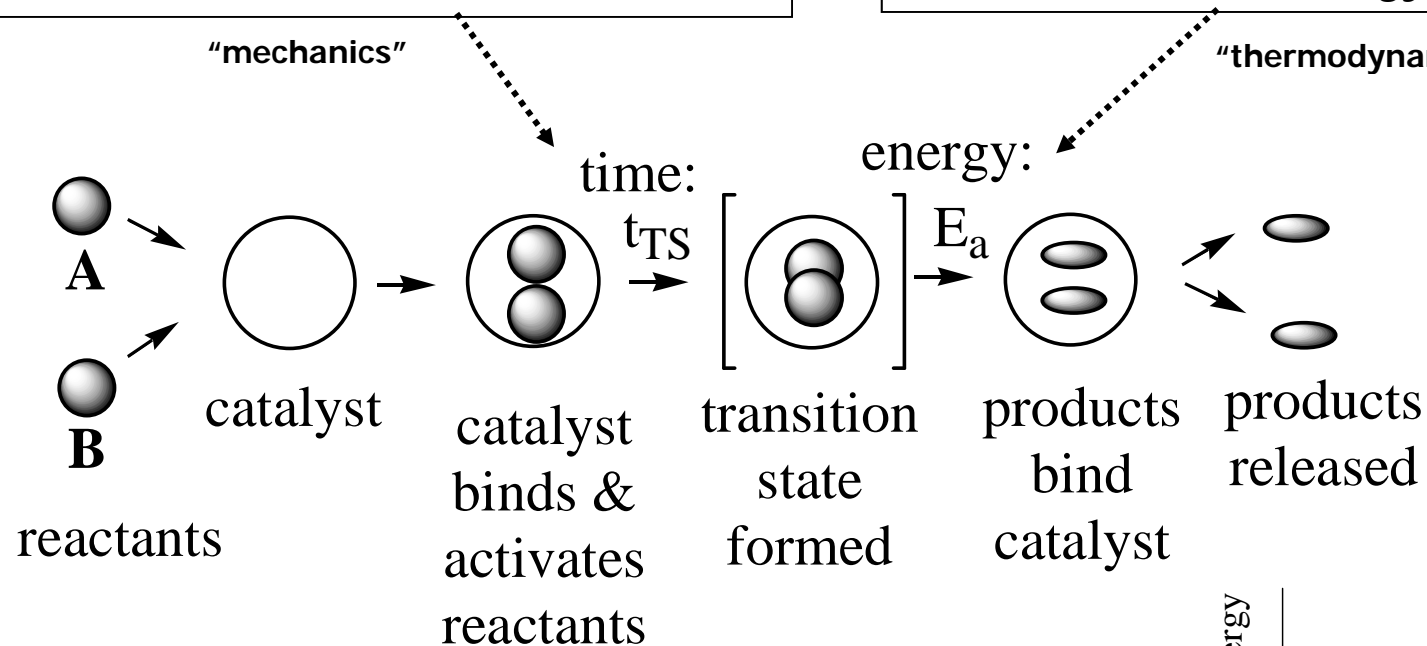
"Mechanical" reaction:



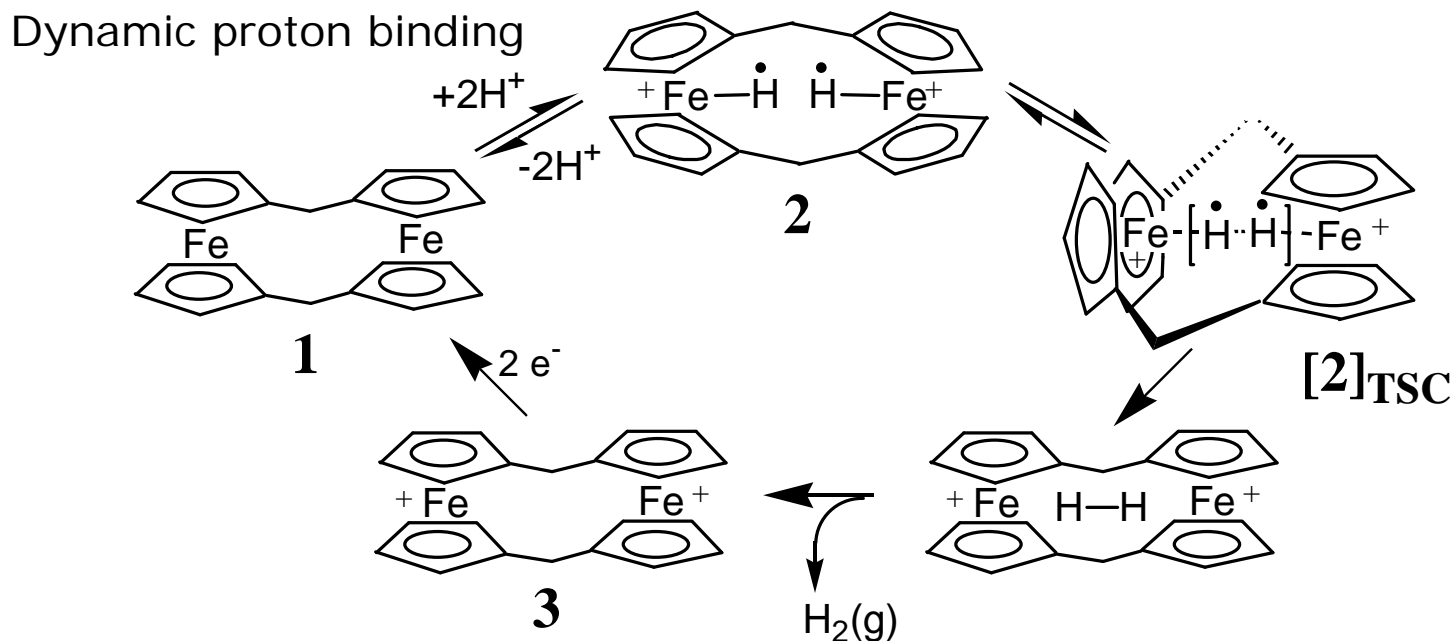
# What Happens in Catalysis?

STEP (1)  
Reactant collision controlled by the  
*"collision frequency" (A)*

STEP (2)  
Product formation controlled by the  
*"activation energy" ( $E_a$ )*



# "Mechanical" Catalysts: H<sub>2</sub> generation

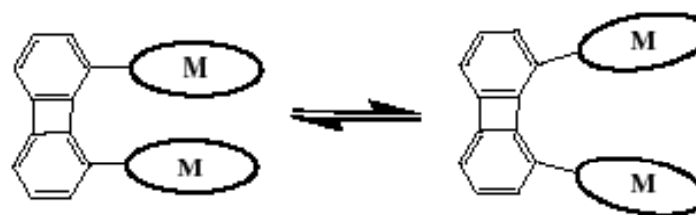
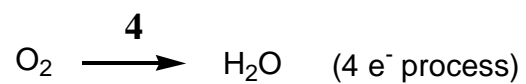
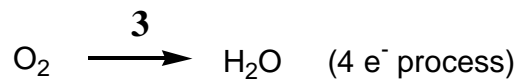
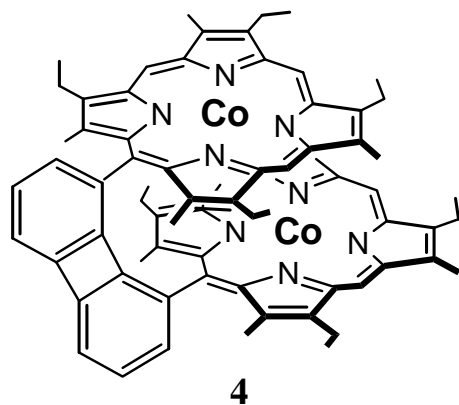
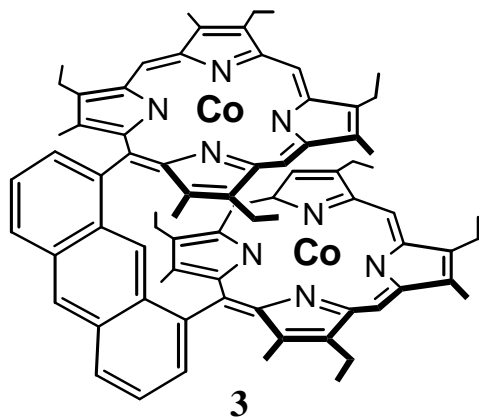


produces 5 molecules H<sub>2</sub> s<sup>-1</sup> catalyst<sup>-1</sup> over at least 5 days of continuous operation

-Two dynamic processes (catalyst flexing and proton binding) which are only *synchronized* if the catalyst flexes rapidly about a structure that *complements the transition state*



# "Mechanical" Catalysts: O<sub>2</sub> reduction



"Pac-Man" Catalyst

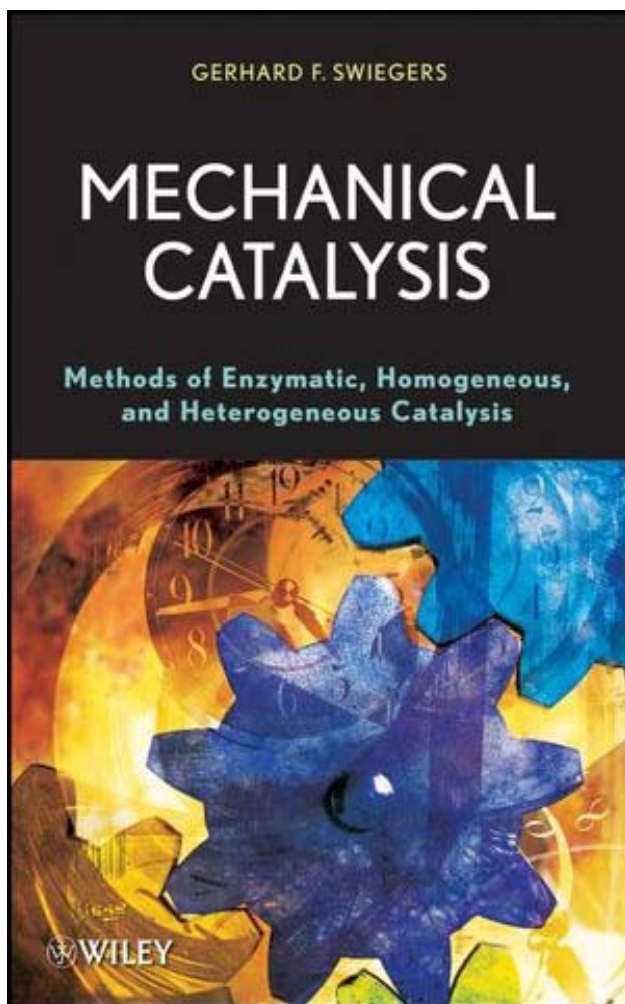
# Some Common Features of “Mechanical” Molecular Catalysts

- (1) Reaction controlled by the *Catalyst-Mediated Collision Frequency* (low *Activation Energy*)
- (2) The maximum catalytic rate depends on the rate of conformational flexing (conformational flexing = the “mechanical impetus”)
- (3) Catalyst typically flexes rapidly about a shape that *complements the transition state*
- (4) Highly efficient and selective form of catalysis (like a machine)
- (5) Michaelis-Menten kinetics

*Chem Eur J* 2009, 15, 4746

• These features also found in many enzymes

QUESTION: Are enzymes mechanical catalysts?

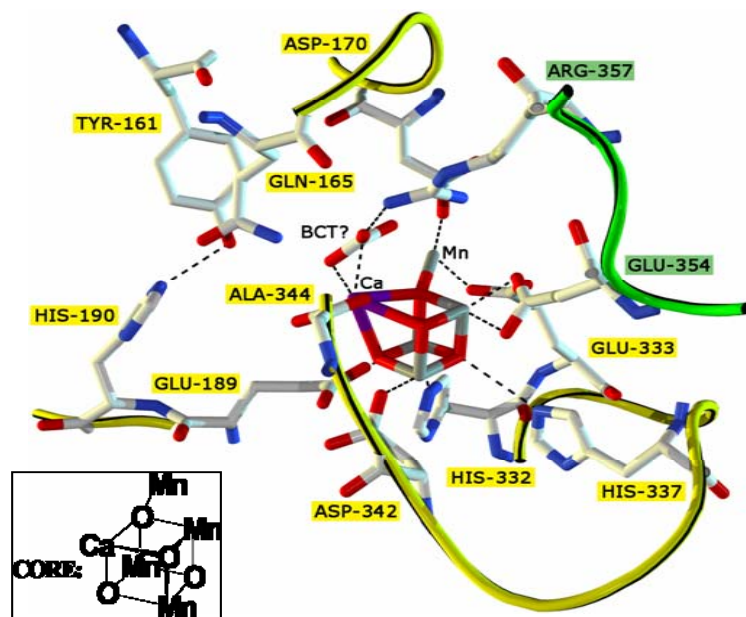


*Mechanical Catalysis: Methods of Enzymatic, Homogeneous, and Heterogeneous Catalysis*

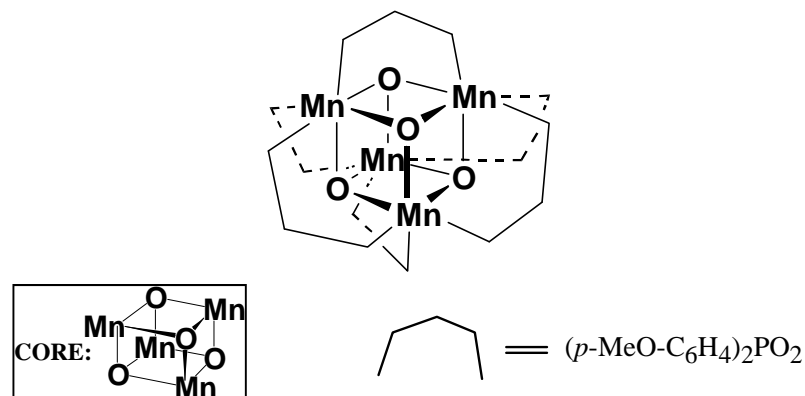
Swiegers, G. F.

John Wiley & Sons, New York, 2008

# Can we Mimic an Enzyme?



Water-Oxidizing Complex of  
Photosystem II  
(PSII-WOC)



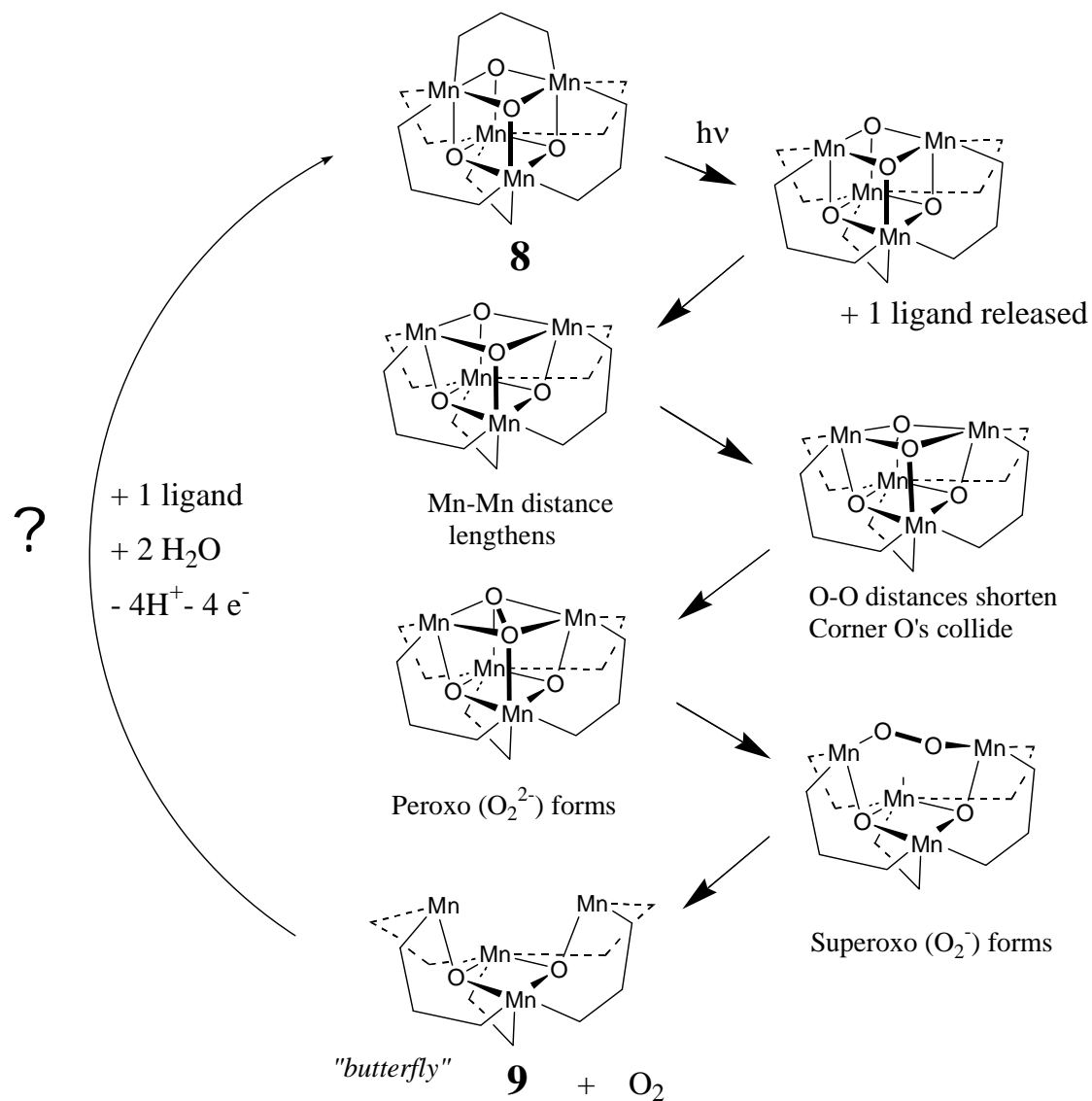
Bio-inspired Mn-oxo *Cubane* Model Complex

G. C. Dismukes, Princeton University

Cubane:

- Shape and structure similar to enzyme active site
- Dynamically self-assembles
- Flexible
- Low activation energy for O<sub>2</sub> release (photolytic)

# Cubane forms O<sub>2</sub> when illuminated

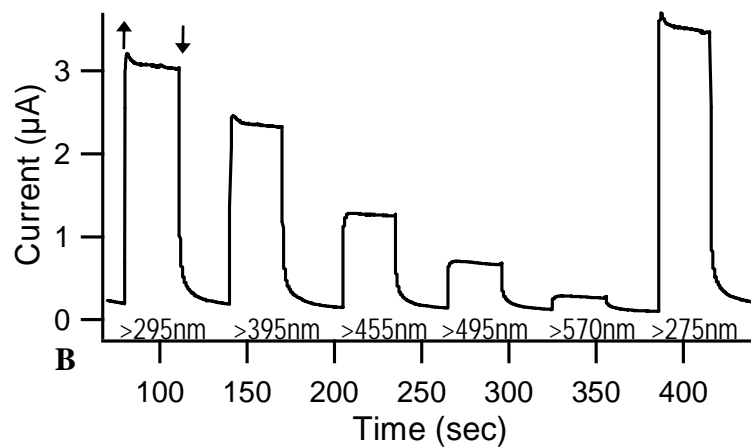
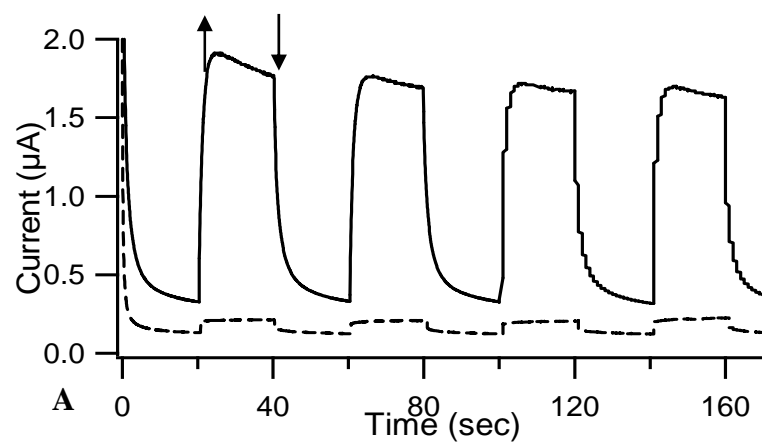


DeAngelis, Carr

# Cubane in Nafion layer on GC electrode

Electrode biased at 1.0 V (vs. Ag/AgCl)

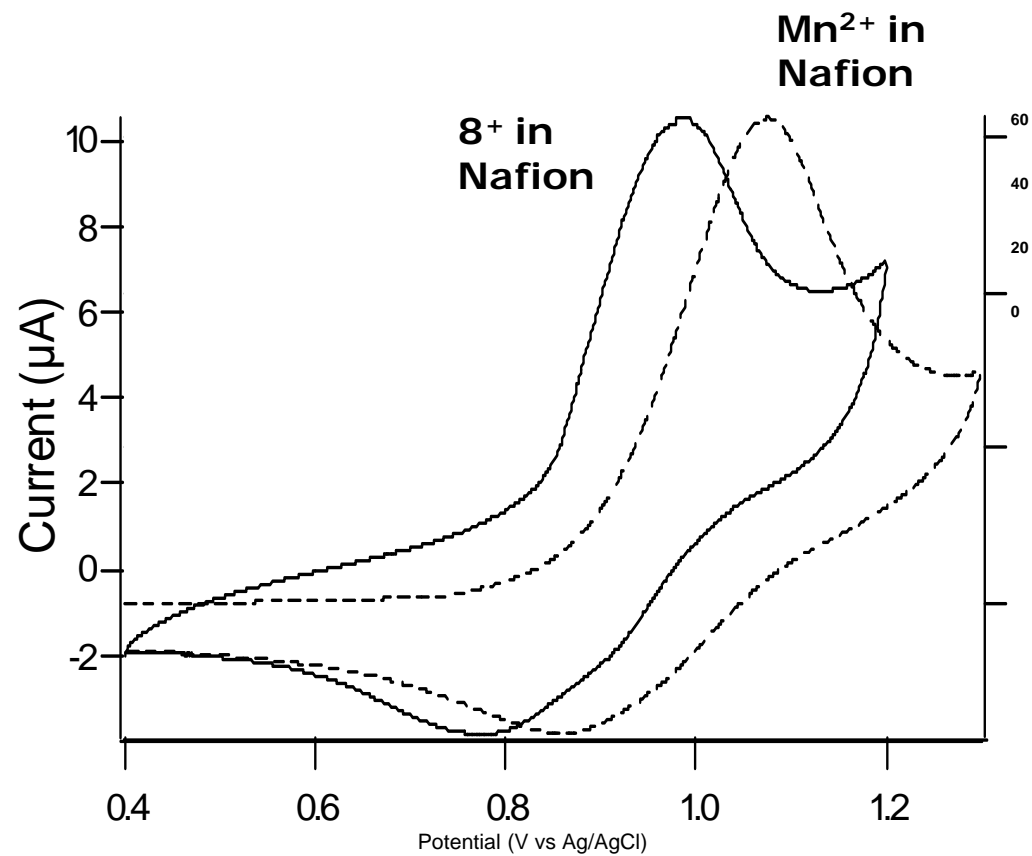
Illuminated at 250-750 nm



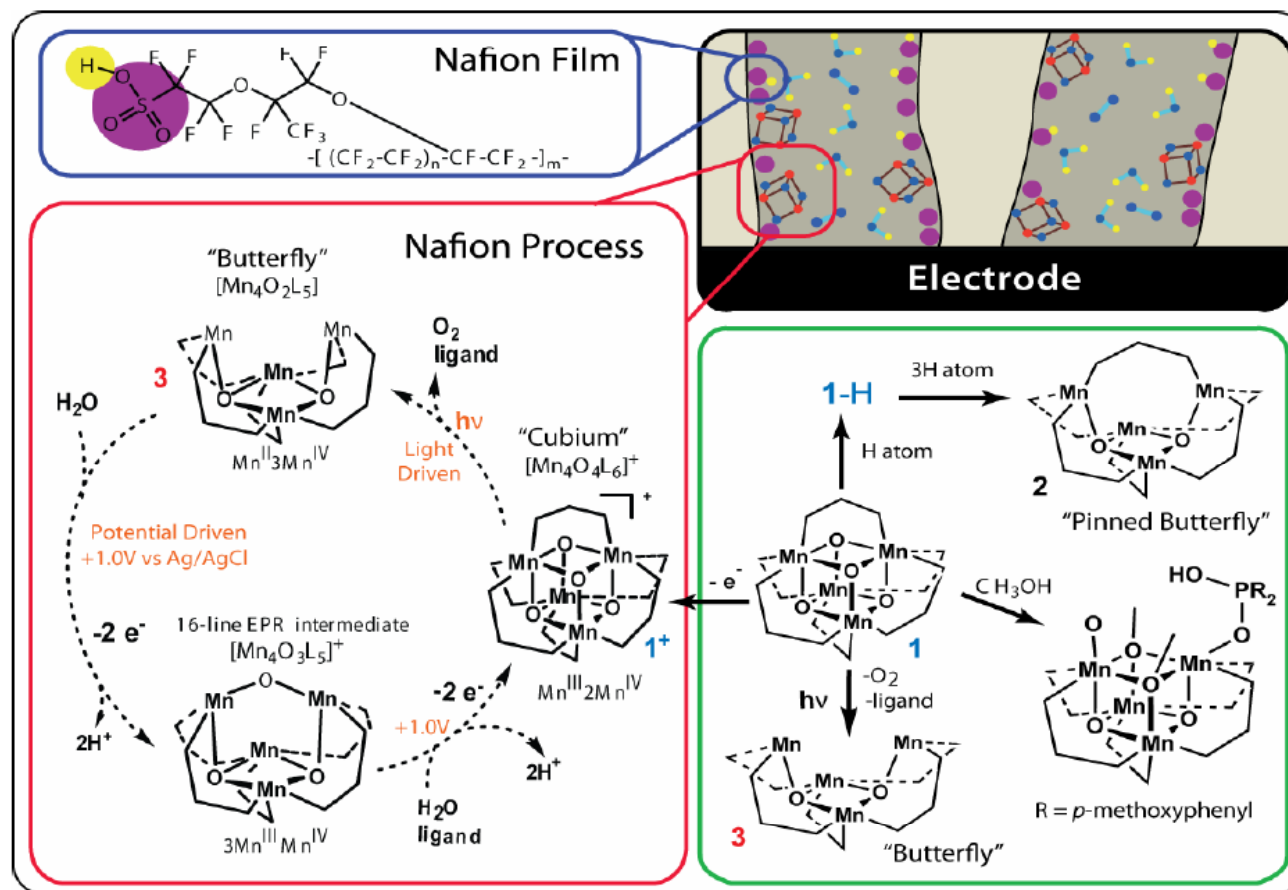
Peak turnover frequency:  
270 molecules  $\text{O}_2$   $\text{h}^{-1}$  catalyst $^{-1}$

Total turnovers:  
>1000 readily achieved

# Cubane<sup>+</sup> ion-exchanged into Nafion: CV



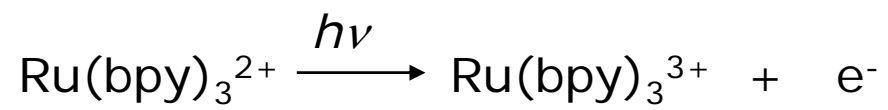
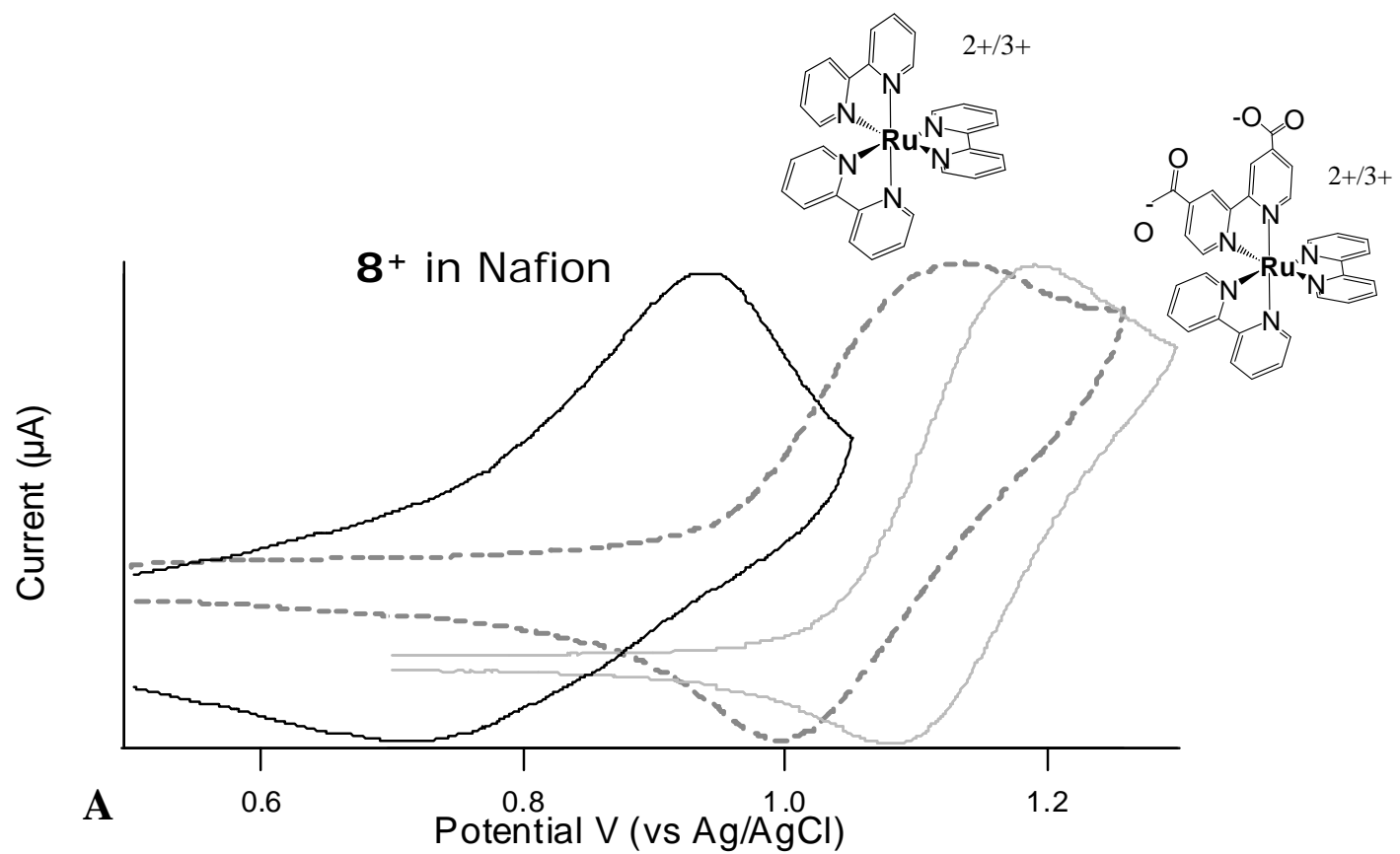
# Proposed Mechanism



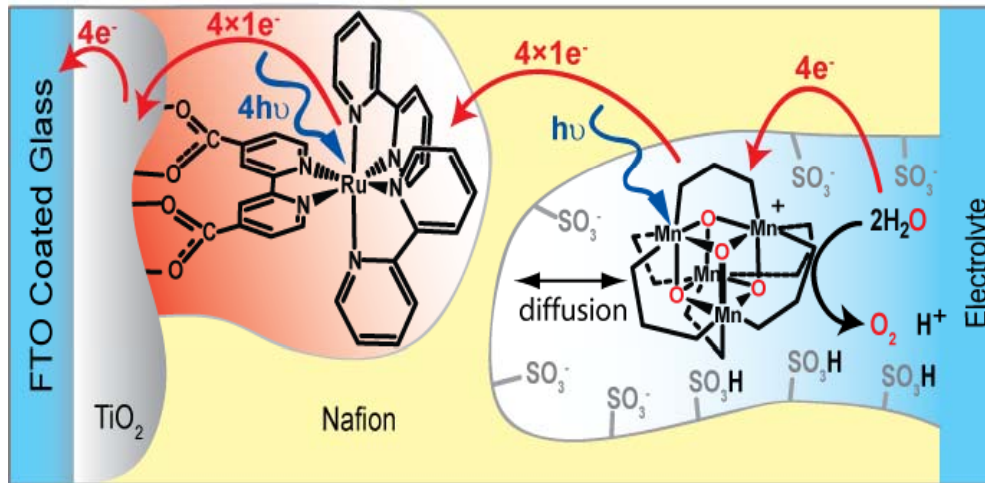
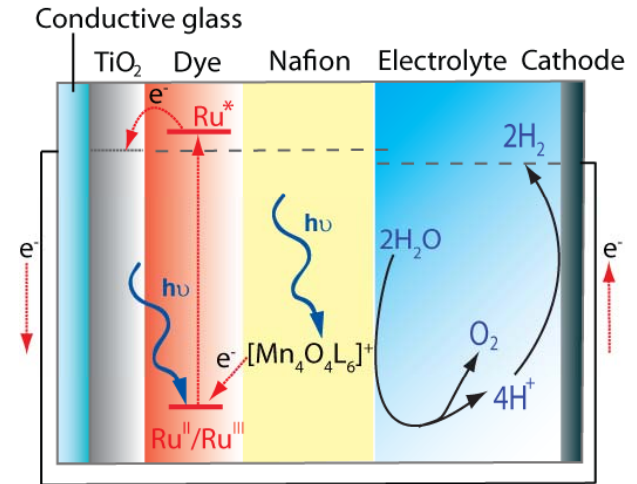
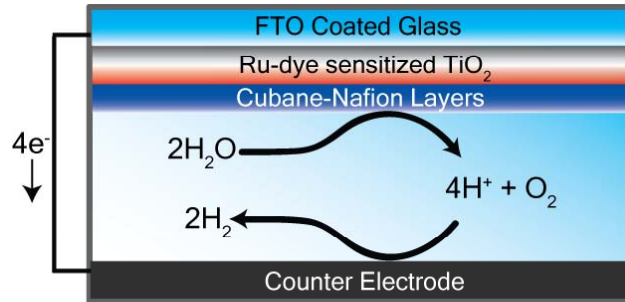
Catalyst dis-assembles and re-assembles under turnover conditions



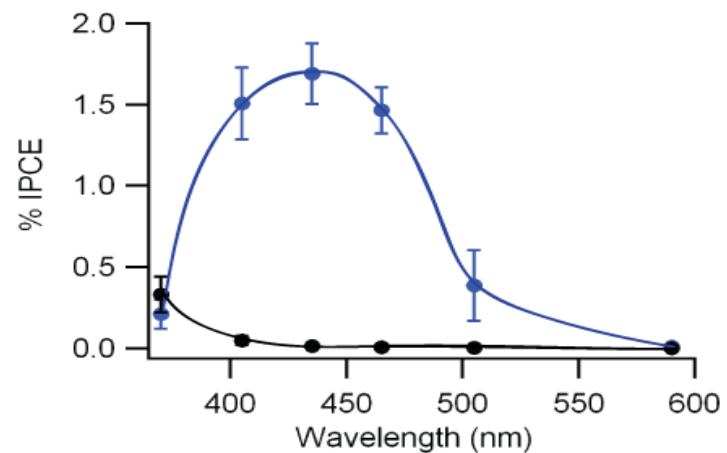
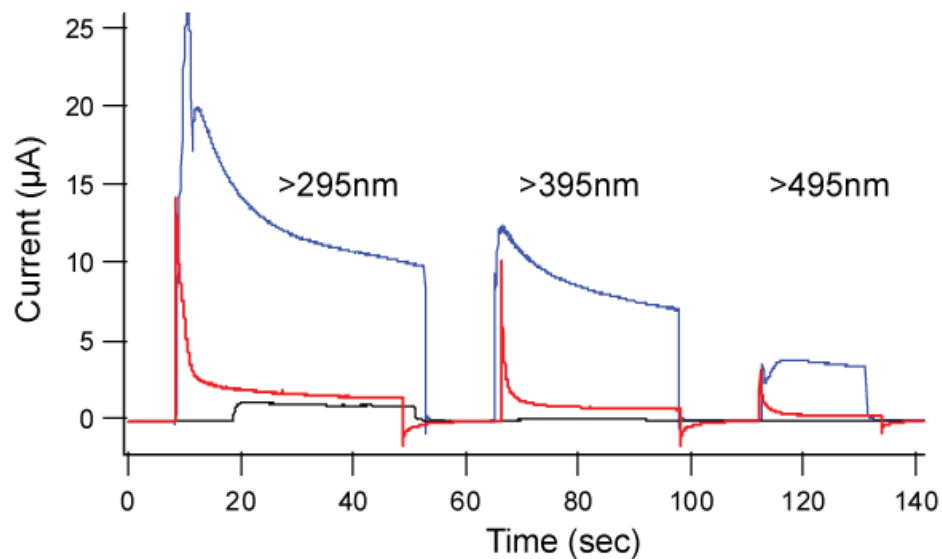
# CV



# Water-Splitting "Graetzel" Cell



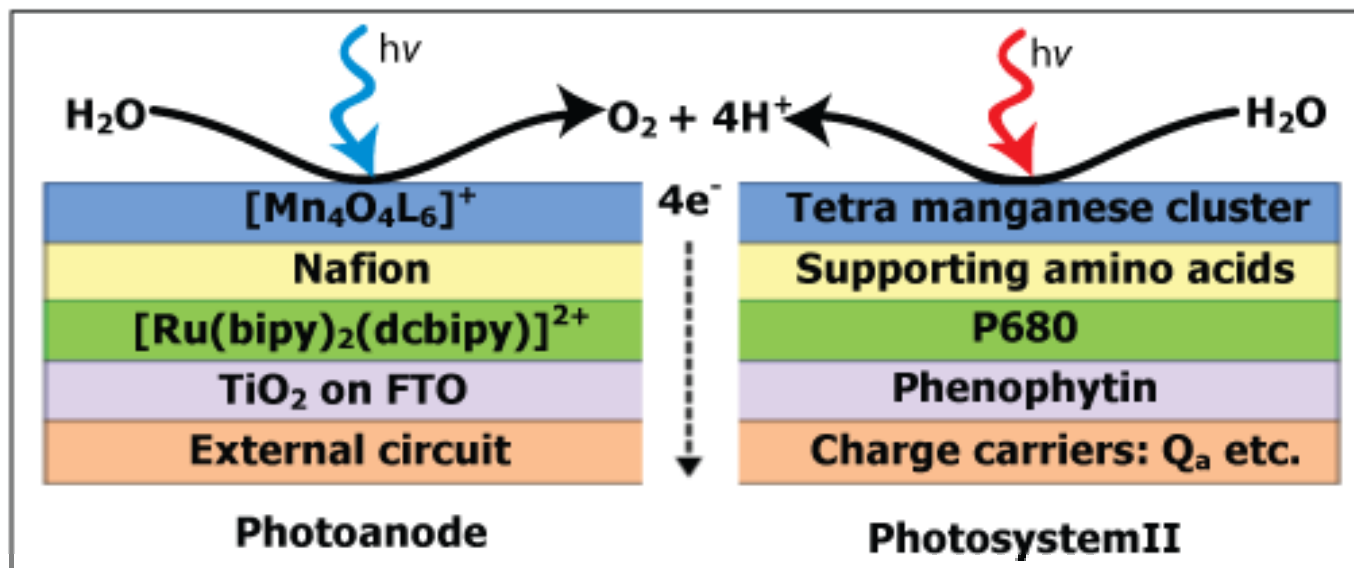
# Water-Splitting “Graetzel” Cell



Uses H<sub>2</sub>O as electrolyte – even impure H<sub>2</sub>O (seawater).  
Eliminates the need for acetonitrile electrolyte which bedevils existing Graetzel cells

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- System splits seawater into pure oxygen (no chlorine formation)
- Spin-off company: “*Cube Catalytics LLC*”  
(funded by New Energy Ventures, New Jersey)



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