

**SOLAR
FUELS**

& NEXT GENERATION
PHOTOVOLTAICS



Dye-Sensitized Photoelectrosynthesis Cells for Solar Fuels

*Energy Frontier Research Center
University of North Carolina at Chapel Hill
November 5, 2010*



ENERGY FRONTIER
RESEARCH CENTER

*The University of North Carolina
at Chapel Hill*

Duke
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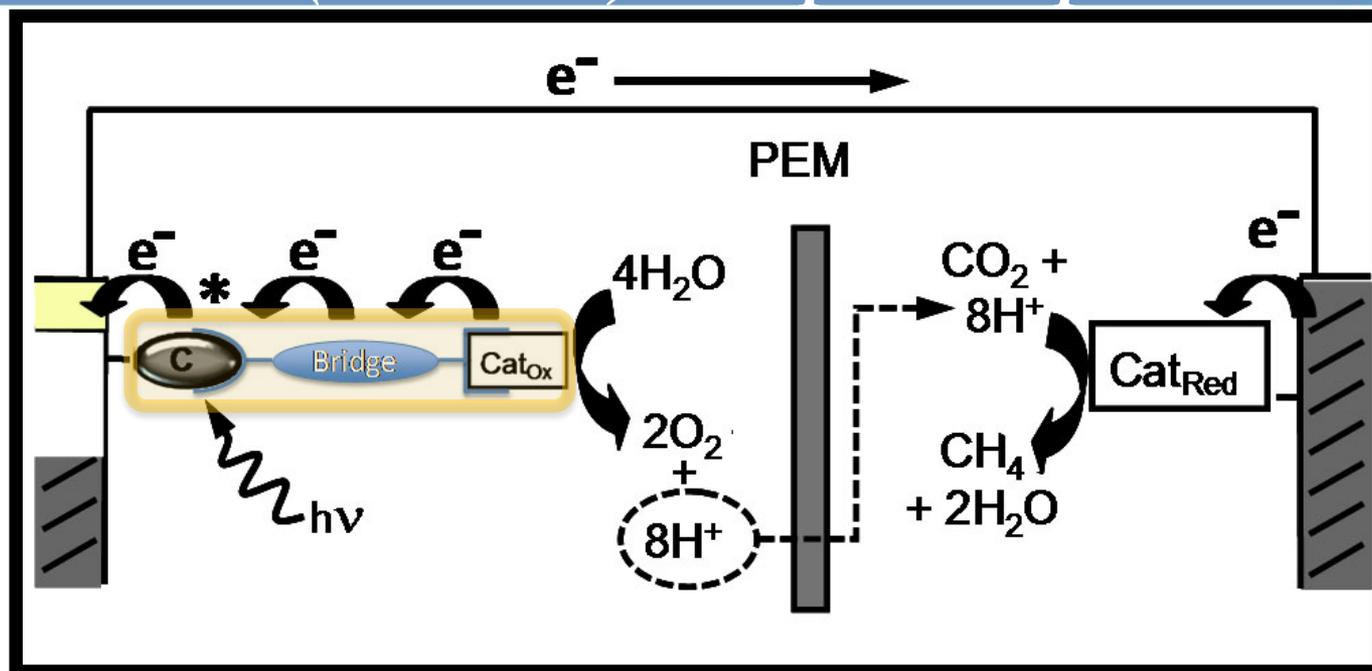


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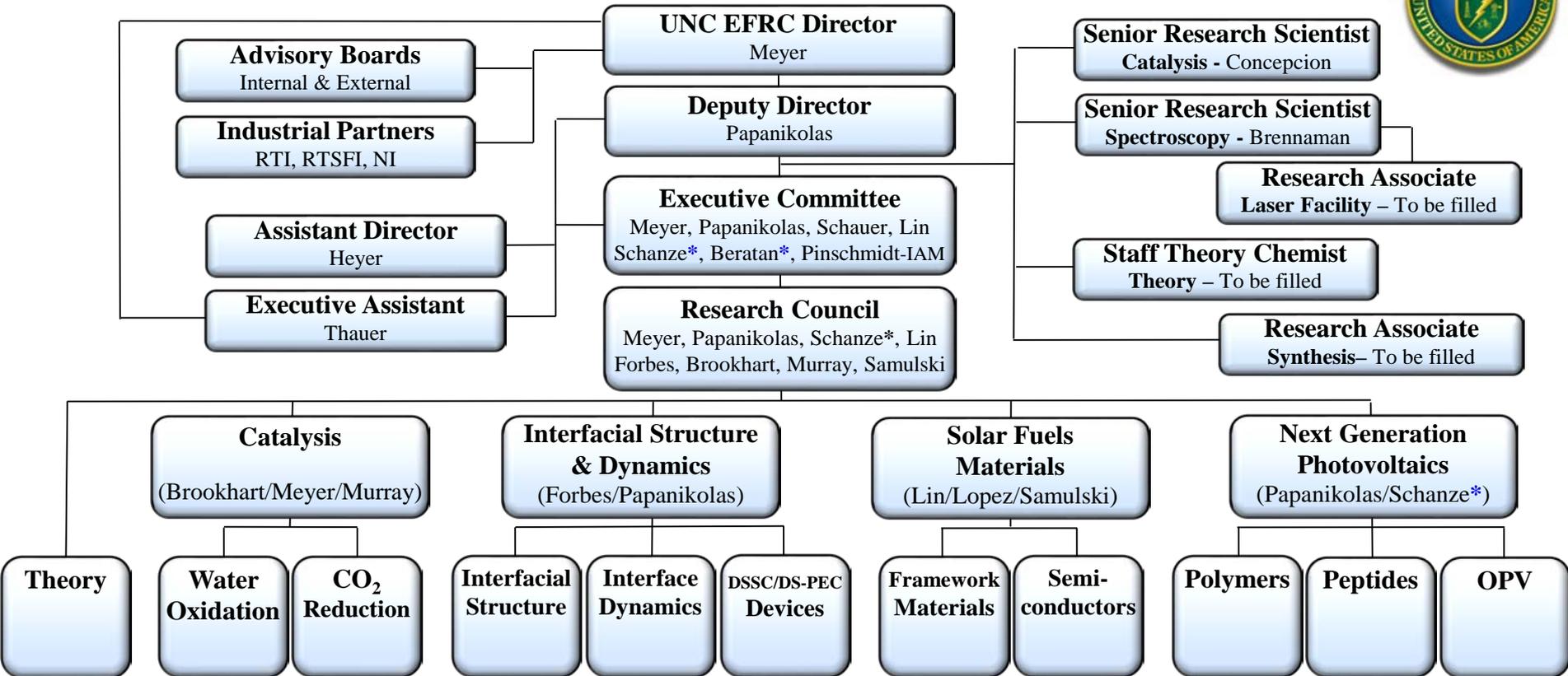
Dye Sensitized Photoelectrosynthesis Cells (DS PEC): Keep it Simple



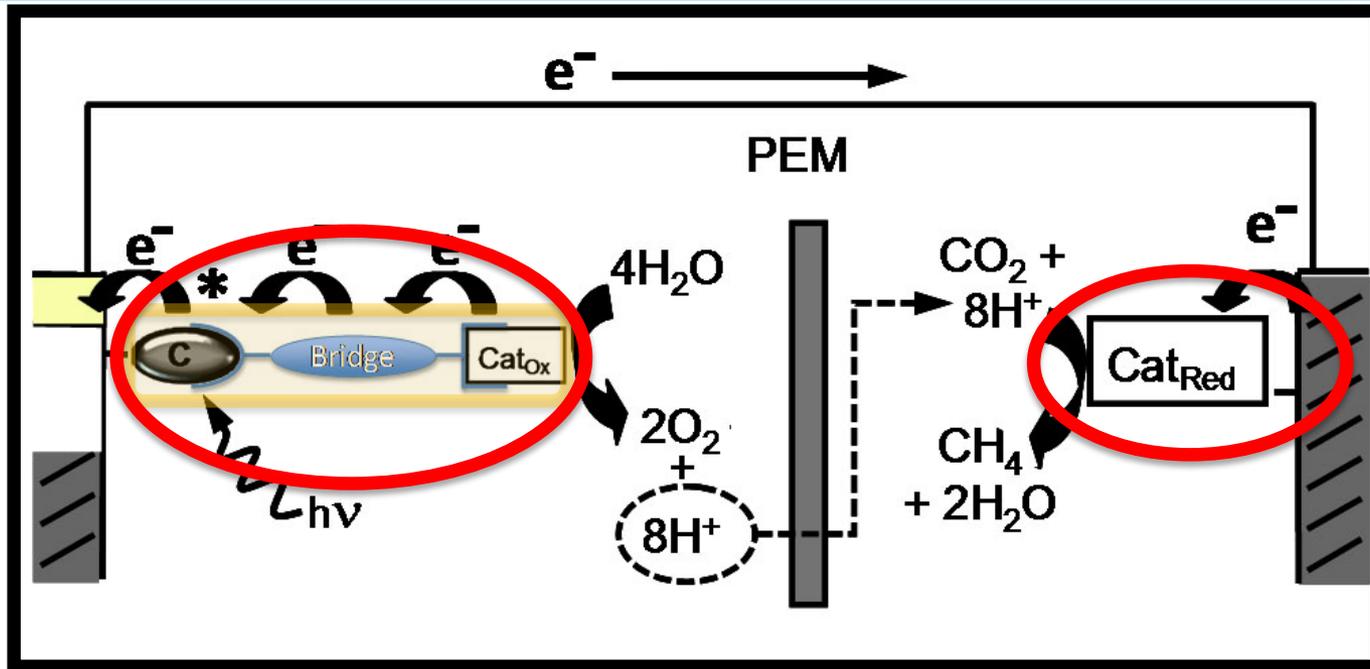
DS PEC : Challenges

- **Rate:** $\sim 10^3 \text{ s}^{-1}$ - exceed the solar flux ($\sim 10 \text{ mA/cm}^2$)
- **Robust:** $> 3 \cdot 10^{10}$ cycles/annum
- **C:** High absorptivity in the Vis-NIR; high $E_{1/2}$ for $\text{C}_{\text{Ox}}^{(n+1)+}/\text{C}_{\text{Red}}^{n+}$
- **Cat_{Ox}:** minimized absorptivity
- **Easy, scalable synthesis**
- **Amenable to incorporation into final devices**

ORGANIZATION CHART



DS PEC: Keep it Simple

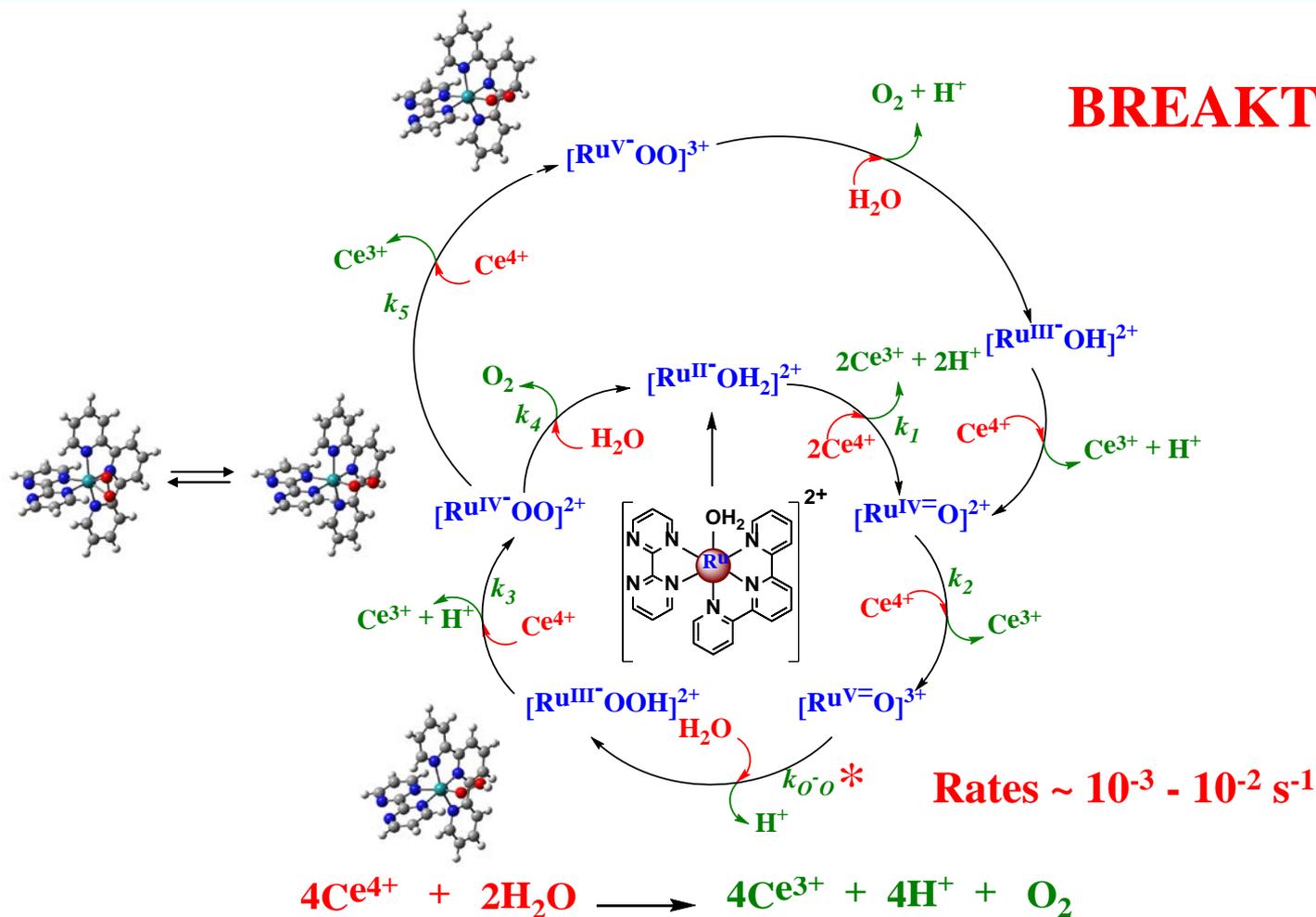


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One Site is Enough

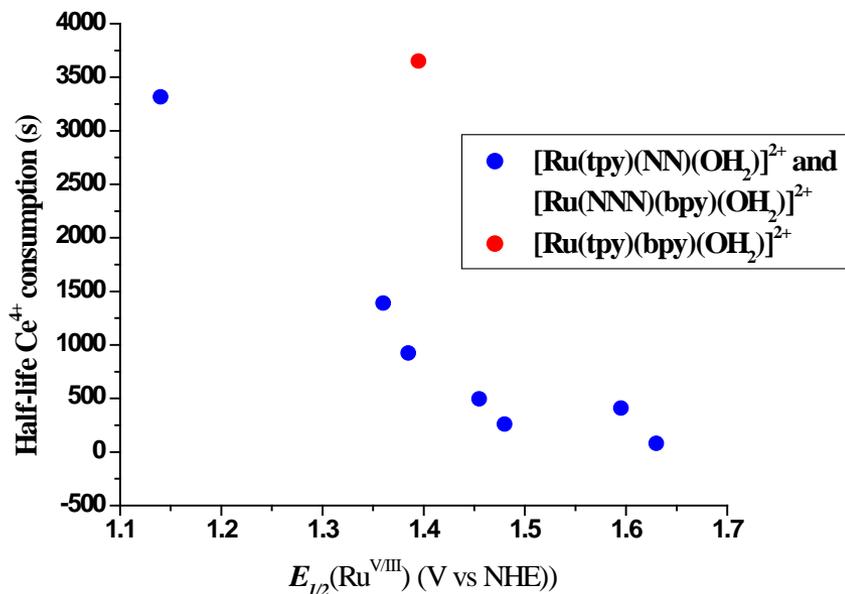
BREAKTHROUGH!



Concepcion *et al.*, *JACS* **2010**, *132*, 1545–1557.

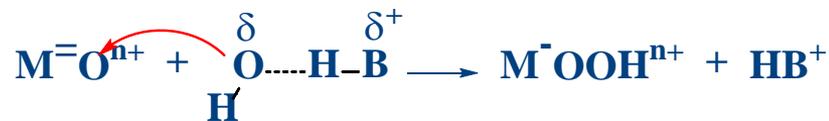
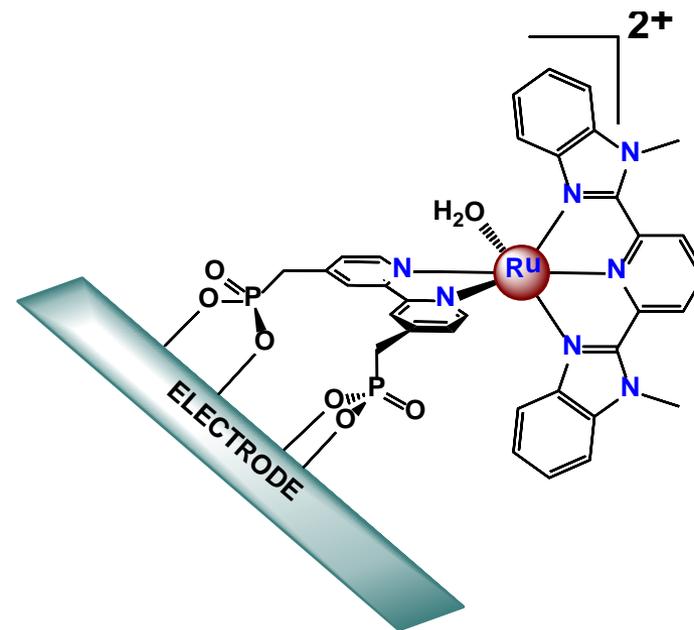
Concepcion *et al.*, *JACS* **2008**, *130*(49), 16462-16463.

Enhance Reactivity



- Tunability by synthesis
- Quantitative understanding of rates and driving forces

Device Configuration

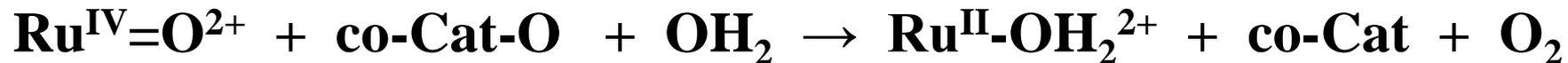


- Rate enhancements of $> 10^4$
- Solution reactivity retained on surfaces

- Water oxidation based on $\text{Ru}^{\text{IV}}=\text{O}^{2+}$:

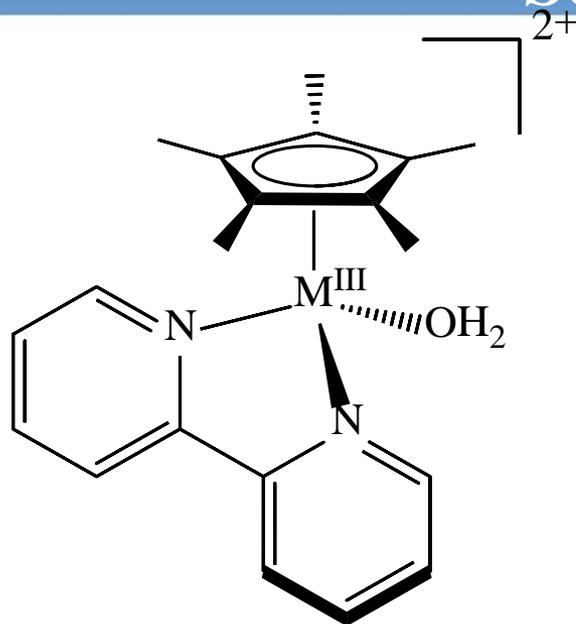


- Two consecutive OAT steps:



- Water oxidation based on *trans*- $\text{Ru}^{\text{VI}}(\text{O})_2^{2+}$:



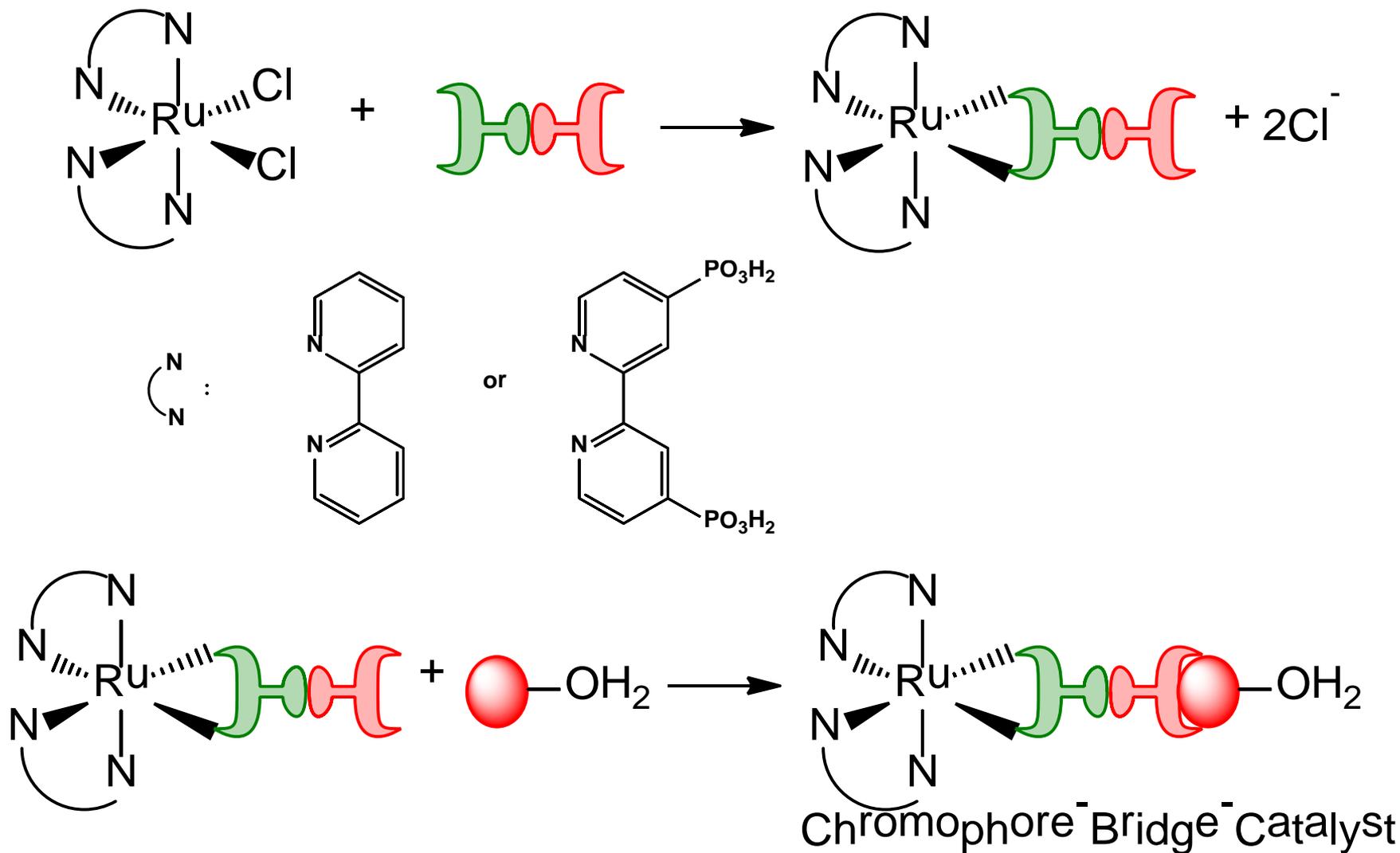


$M = Ir, Ru, Co$

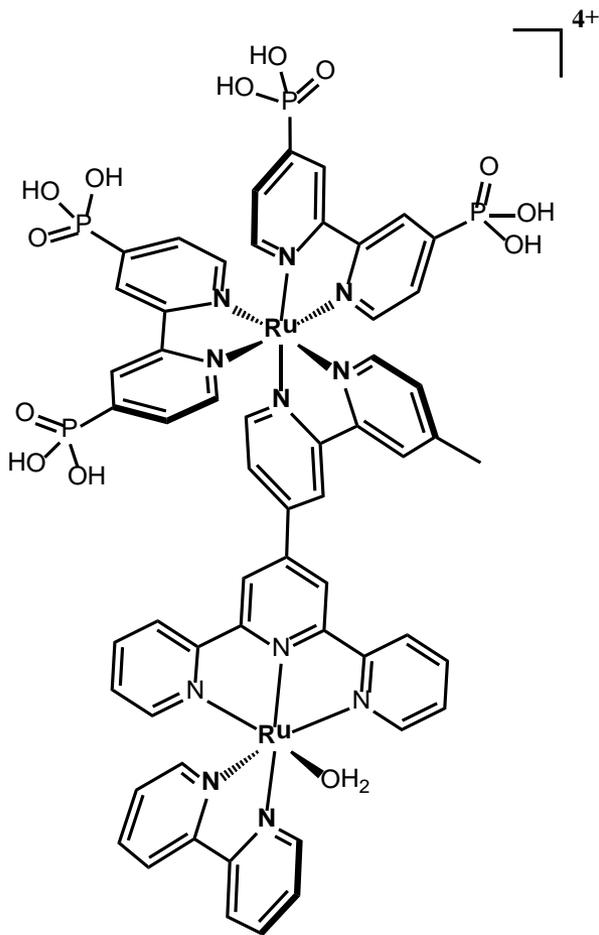
- Electrochemistry: what are the relevant couples?
- pH-dependence
- Water oxidation catalysts?
- Assisted pathways

TOF ~ 150 - 410 s⁻¹ !

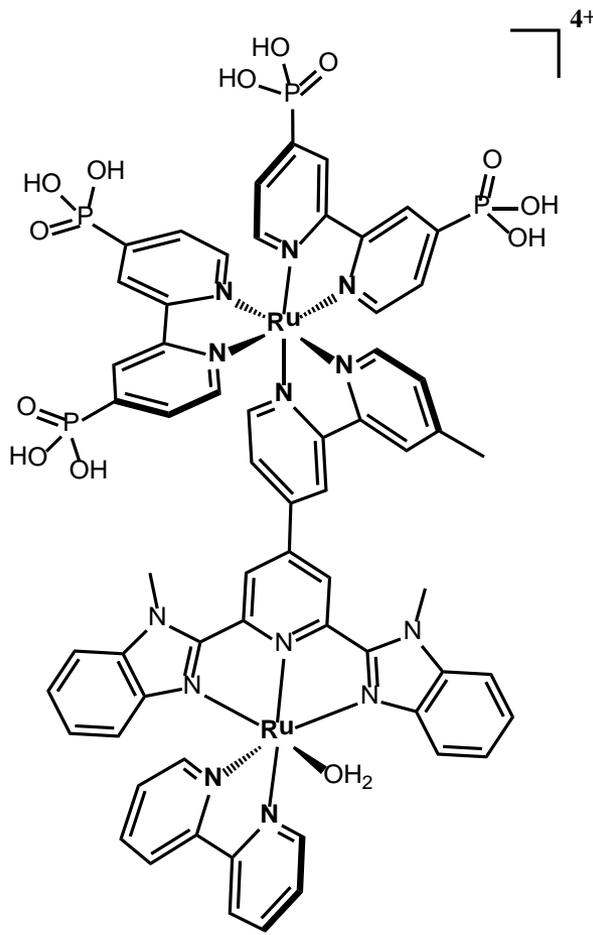
Synthetic Strategy for Assemblies



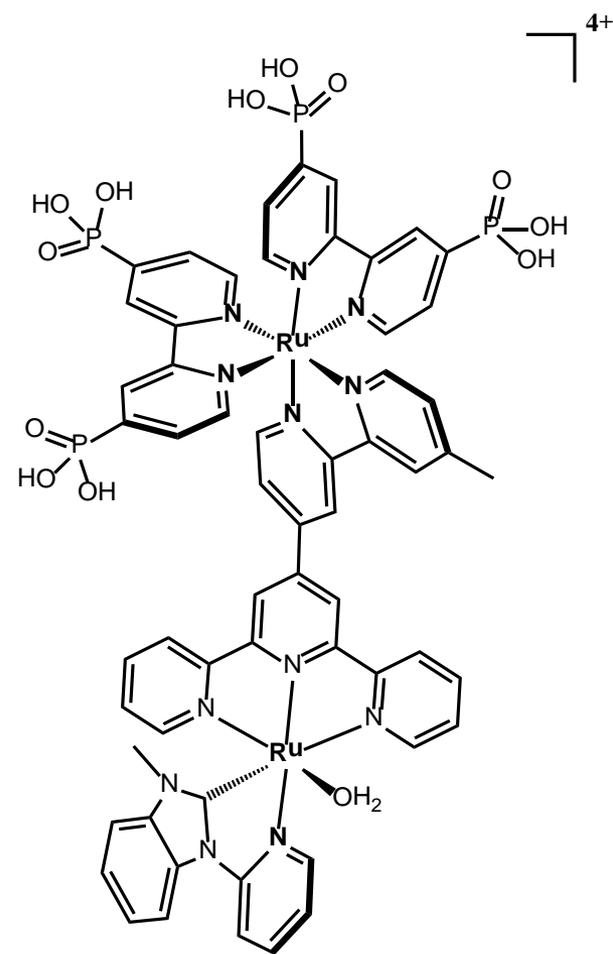
Targets/Examples of Assemblies



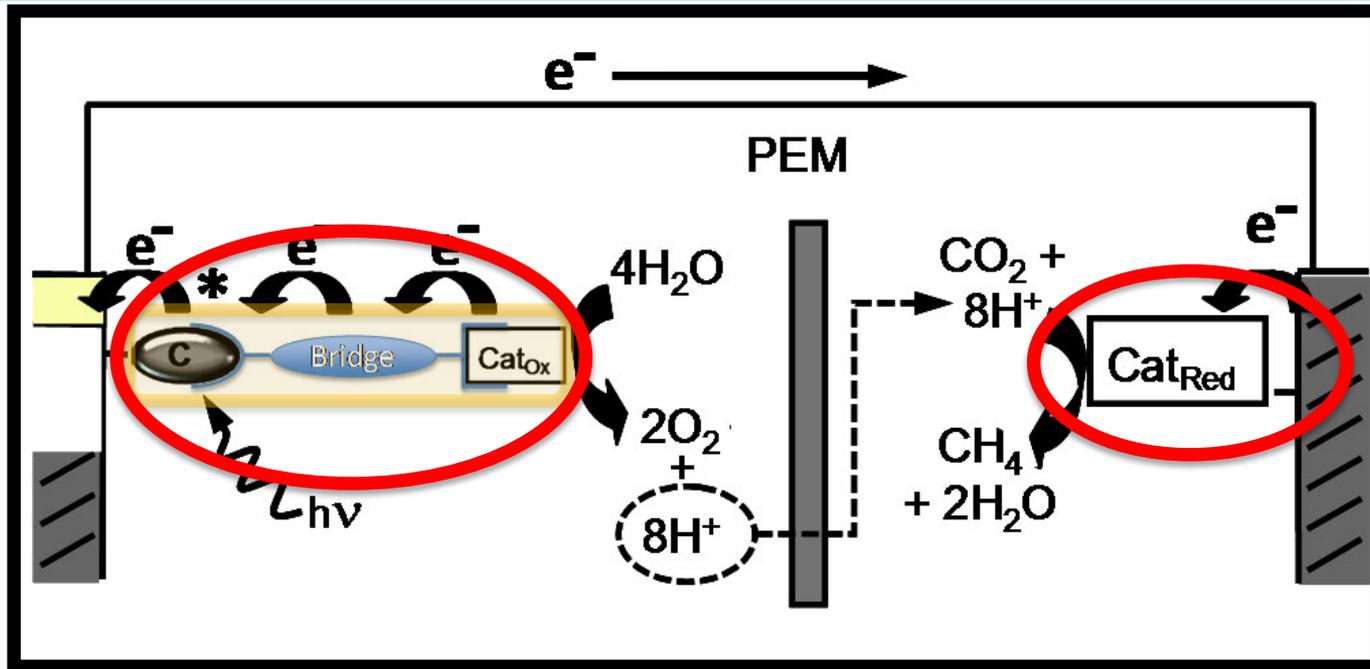
1



2



3

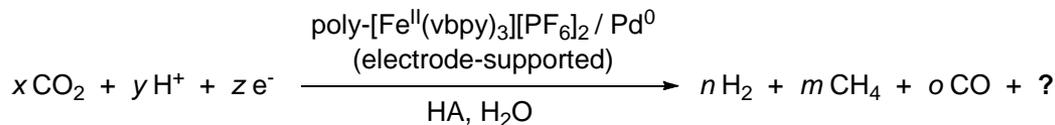


DS PEC Water Oxidation Catalysis: Challenges

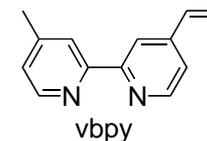
- **Rate:** $\sim 10^3 \text{ s}^{-1}$ - exceed the solar flux ($\sim 10 \text{ mA/cm}^2$)
- **Robust:** $> 10^9$ turnovers
- **C:** High absorptivity in the Vis-NIR; high $E_{1/2}$ for $\text{Ru}^{3+/2+}$
- **Cat_{Ox}:** minimized absorptivity
- **Easy, scalable synthesis**
- **Amenable to incorporation into final devices**

Electrochemical CO₂ Reduction Catalyzed by Polymer Supported, Nanostructured Pd(0)

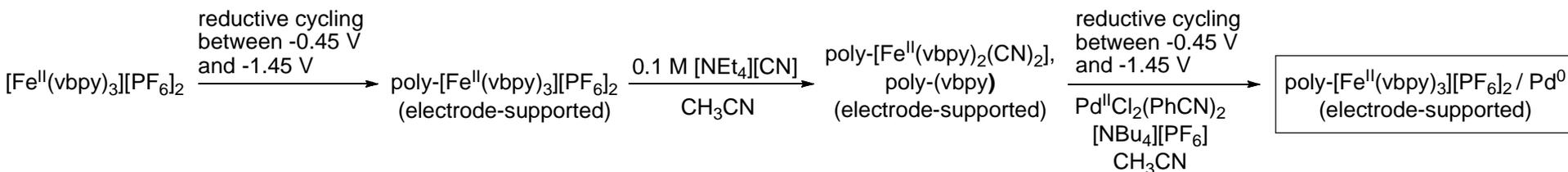
Electrochemical CO₂ Reduction Catalysis



Potentials reported vs. NHE



Catalyst Generation

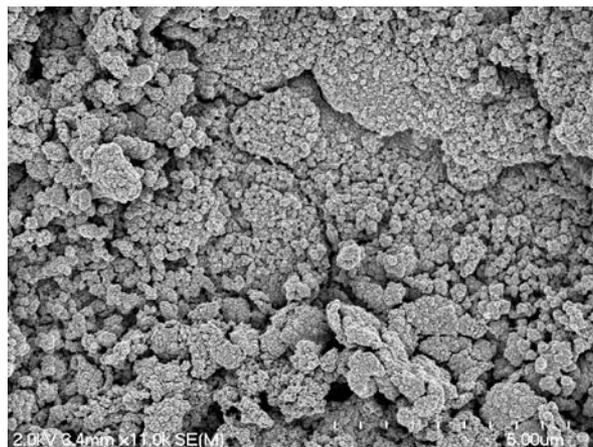


Bakir, M.; Sullivan, B. P.; MacKay, S.; Linton, R. W.; Meyer, T. J. *Chem. Mater.* **1996**, *8*, 2461-2467.

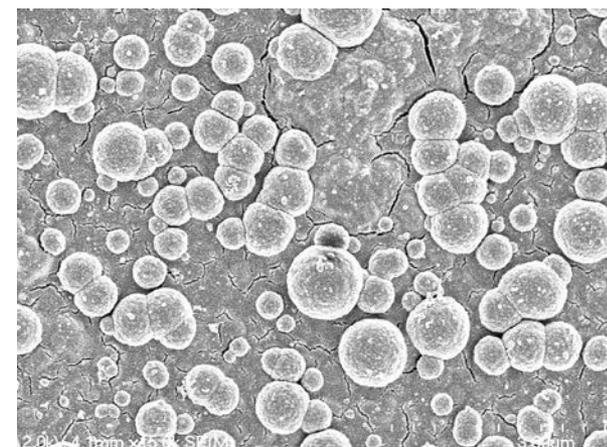
- High surface area Pd(0) electrodes
 - Allow rapid product generation
 - The polymer stabilizes them and keeps them on the electrode surface
- Small diameter particles could catalyze the generation of unique product mixtures.

Pd(0) Morphology: Controlled by Electrodeposition Scan Rate

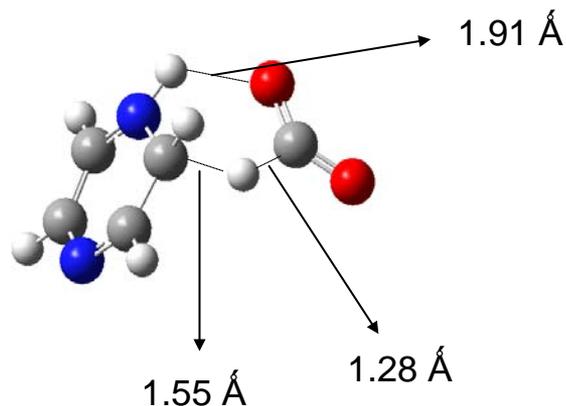
10 mV/s



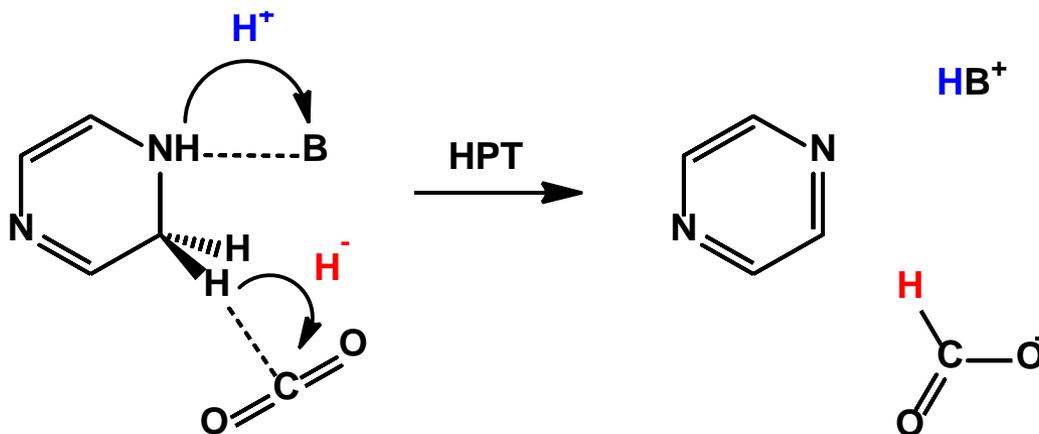
500 mV/s



1,2-dihydropyrazine



DFT, B3LYP, 6-31G
Solvent: IEFPCM, water



- ✓ *Catalyst tunability by synthesis*
- ✓ *Quantitative understanding of rates and driving forces*
- ✓ *Rate enhancements of $> 10^4$ with base-assisted catalysis*
- ✓ *Solution reactivity retained on surfaces*
- ✓ *New catalysts, new pathways for water oxidation*
- ✓ *Synthesized and began studies of assemblies for DS PEC*
- ✓ *PCHT and HPT pathways*
- ✓ *Synthesized and characterized hydride donors*
- ✓ *Initial studies in acetone and CO_2 reduction are underway*