Direct Solar CO_2 for Formic Acid Conversion Using a Biological/Organic Photochemical Half-Cell

ARPA-E Direct-Solar Fuel Technologies Workshop

October 21, 2009

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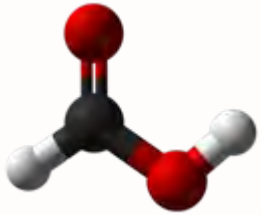
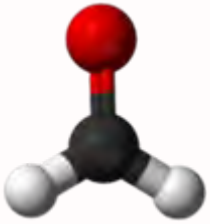
Direct Reduction of Carbon Dioxide

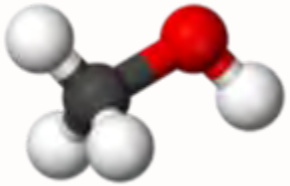
$CO_2 + 2\ e^- + 2H^+ \longleftrightarrow CH_2O_2$ **Formic Acid**



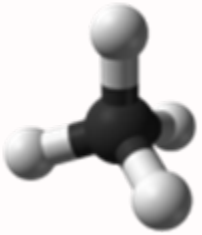
$CH_2O_2 + 2\ e^- + 2H^+ \longleftrightarrow CH_2O + H_2O$ **Formaldehyde**



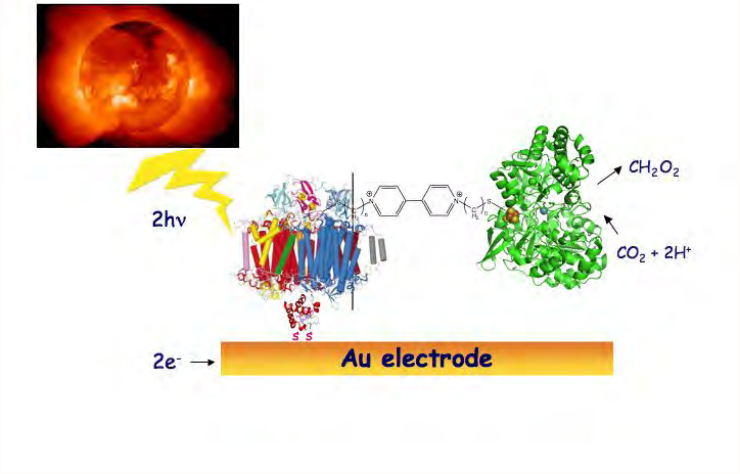
$CH_2O + 2\ e^- + 2H^+ \longleftrightarrow CH_3OH$ **Methanol**



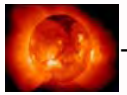
$CH_3OH + 2\ e^- + 2H^+ \longleftrightarrow CH_4 + H_2O$ **Methane**



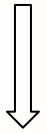
Formic Acid as Fuel



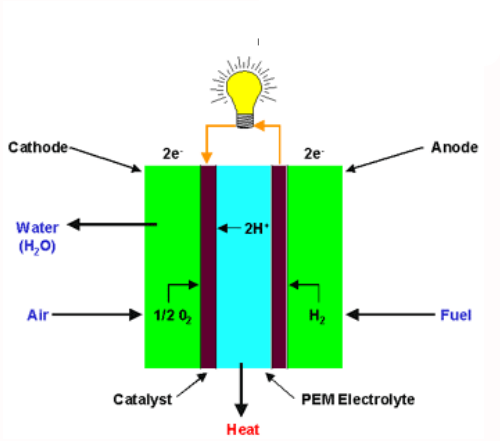
Light-induced Generation
Of Formic Acid from
Carbon Dioxide

$CO_2 + 2H^+ + 2e^- +$  $\rightarrow H_2CO_2$

Formic Acid As
A Storage Medium



$H_2CO_2 \rightarrow CO_2 + 2H^+ + 2e^- +$ 



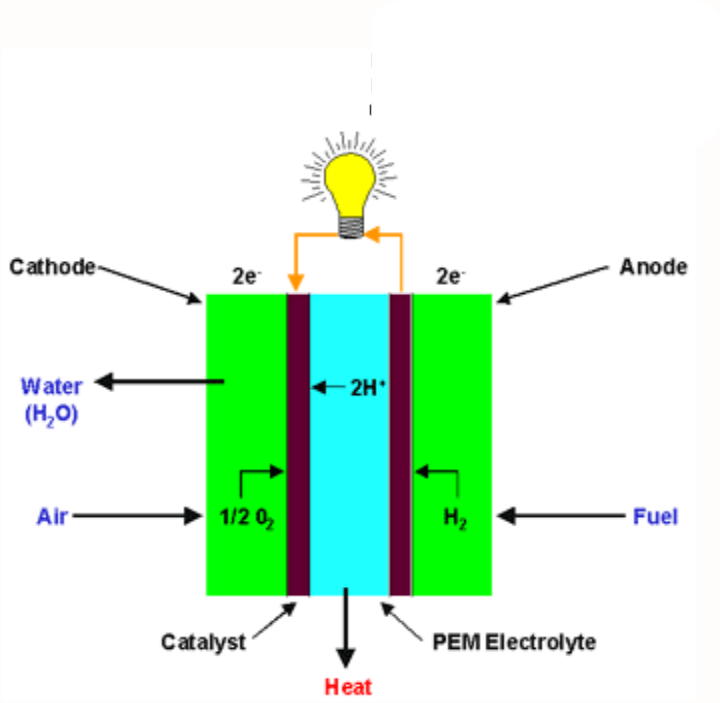
Generation of Electricity
From Direct
Formic Acid Fuel Cell

Formic Acid

Standard Enthalpy of Combustion, formic acid	–255 kJ/mol
Standard Enthalpy of Combustion, methanol	–715 kJ/mol

Standard Biochemical Midpoint Potential

$CO_2 + 2H^+ + 2e^- \longleftrightarrow CH_2O_2$	-420 mV
$2H^+ + 2e^- \longleftrightarrow H_2$	-420 mV



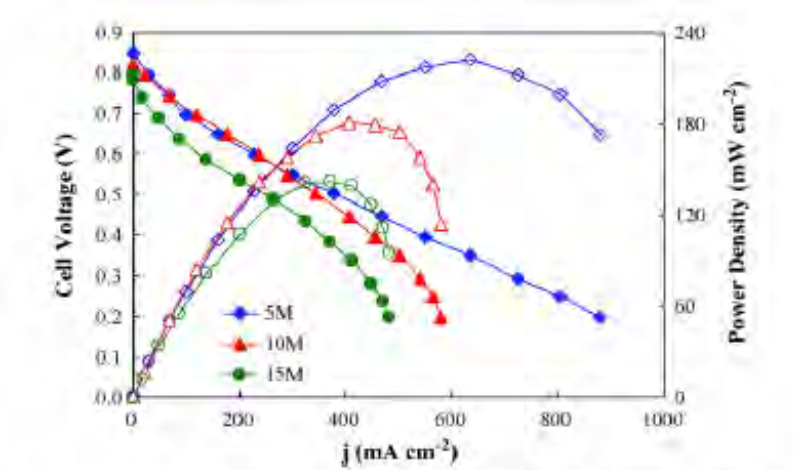


Fig. 5. Cell voltage and power density were plotted as a function of the current density using 5, 10 and 15 M formic acids. The formic acids and air were fed to the anode at a flow rate of 1 ml min^{-1} and 400 sccm, respectively, at 30 °C. The dry air was used without applying any backpressure.

Reversible interconversion of carbon dioxide and formate by an electroactive enzyme

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*Medical Research Council Dunn Human Nutrition Unit, Wellcome Trust/MRC Building, Hills Road, Cambridge CB2 0XY, United Kingdom; †Laboratory of Microbiology, Dreijenplein 10, 6703 HB Wageningen, The Netherlands; and ‡British Antarctic Survey, Natural Environment Research Council, Cambridge CB3 0ET, United Kingdom

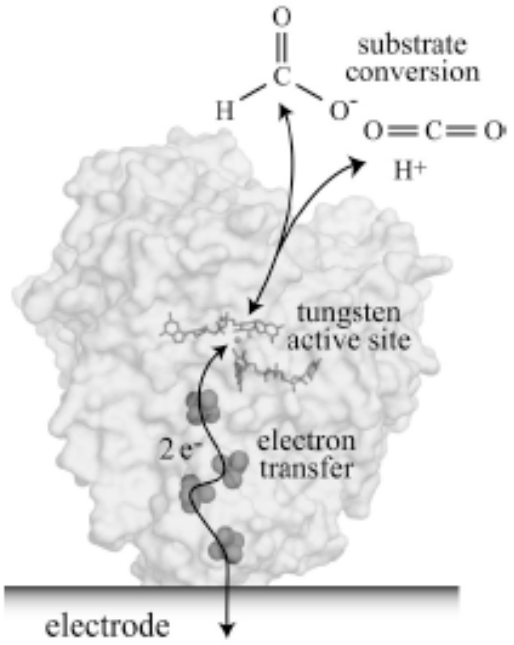


Fig. 1. Schematic representation of the electrocatalytic interconversion of CO_2 and formate by a formate dehydrogenase adsorbed on an electrode surface. Two electrons are transferred from the electrode to the active site (buried inside the insulating protein interior) by the iron–sulfur clusters, to reduce CO_2 to formate, forming a C–H bond. Conversely, when formate is oxidized, the two electrons are transferred from the active site to the electrode. The structure of FDH1 (which contains at least nine iron–sulfur clusters) is not known, so the structure shown is that of the tungsten-containing formate dehydrogenase from *Desulfovibrio gigas* [PDB ID code 1H0H (12)].

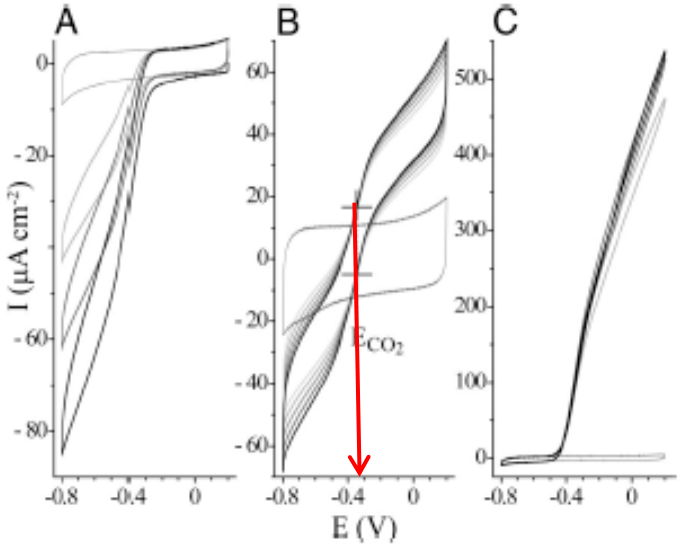
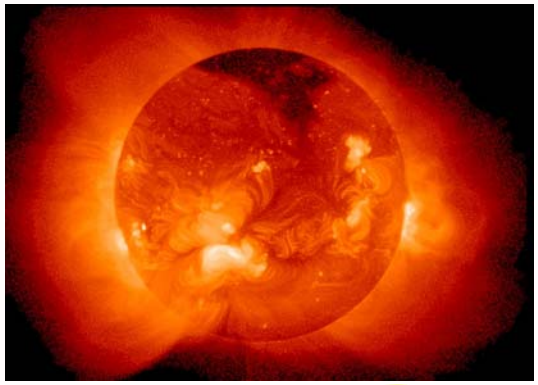
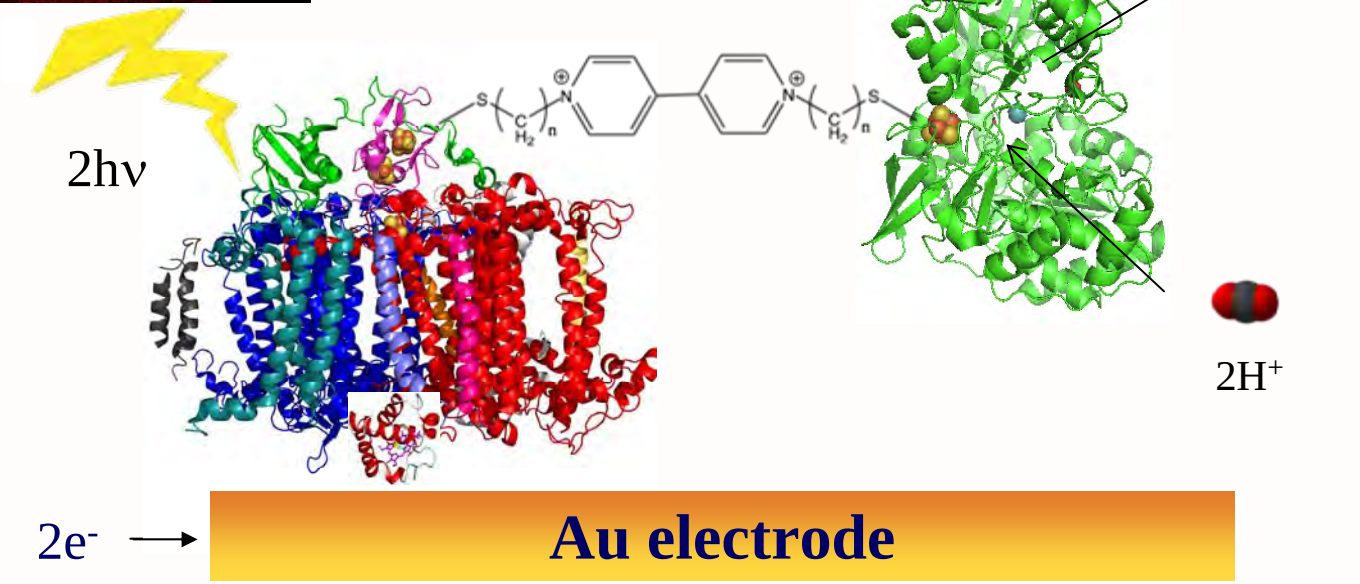


Fig. 2. Electrocatalytic voltammograms showing CO_2 reduction and formate oxidation by FDH1. Shown are the reduction of 10 mM CO_2 (pH 5.9) (*A*); electrocatalysis in 10 mM CO_2 and 10 mM formate (pH 6.4) (*B*), showing the points of intersection (marked with crosses) that define the reduction potential for the interconversion of CO_2 and formate; and the oxidation of 10 mM formate (pH 7.8) (*C*). The first voltammetric cycles are shown in black, subsequent cycles are in gray; background cycles recorded in the absence of substrate are also shown (gray). Note that the background cycle in *B* is offset slightly from the catalytic scans because of variation in the electrode capacitance. Substrates were added as sodium formate or sodium carbonate. For *A* and *C*, 25 mV s^{-1}, for *B*, 100 mV s^{-1}; 37°C, electrode rotation 1,000 rpm.

Project Goal

To use sunlight to drive the formation of H_2CO_2 from CO_2 by tethering FDH to Photosystem I using a molecular wire



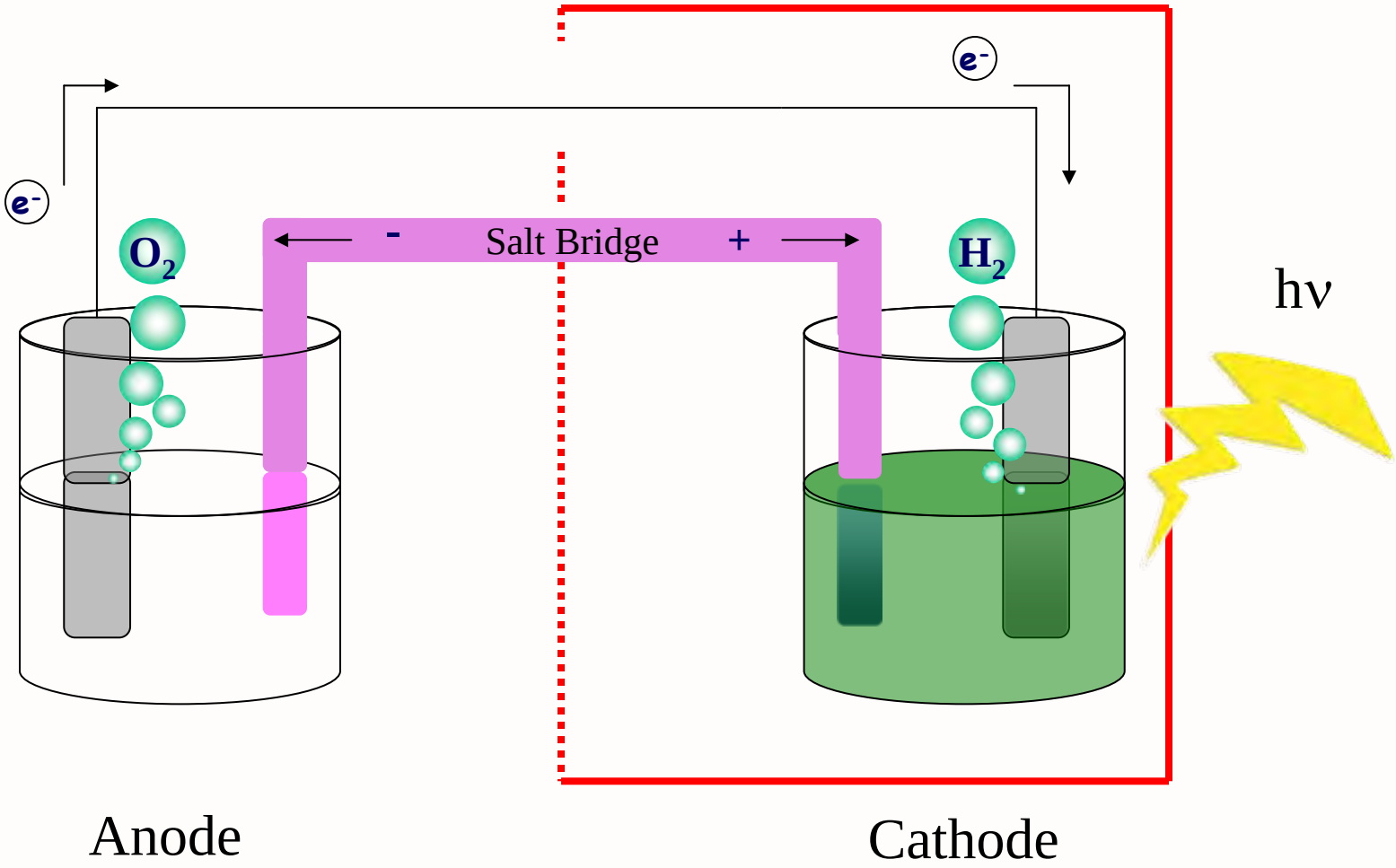


Light-Driven Electrolysis

Overall Reaction: $2H_2O + 8h\nu \rightarrow 2H_2 + O_2$

Anodic half reaction: $2(H_2O + 2h\nu \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-)$

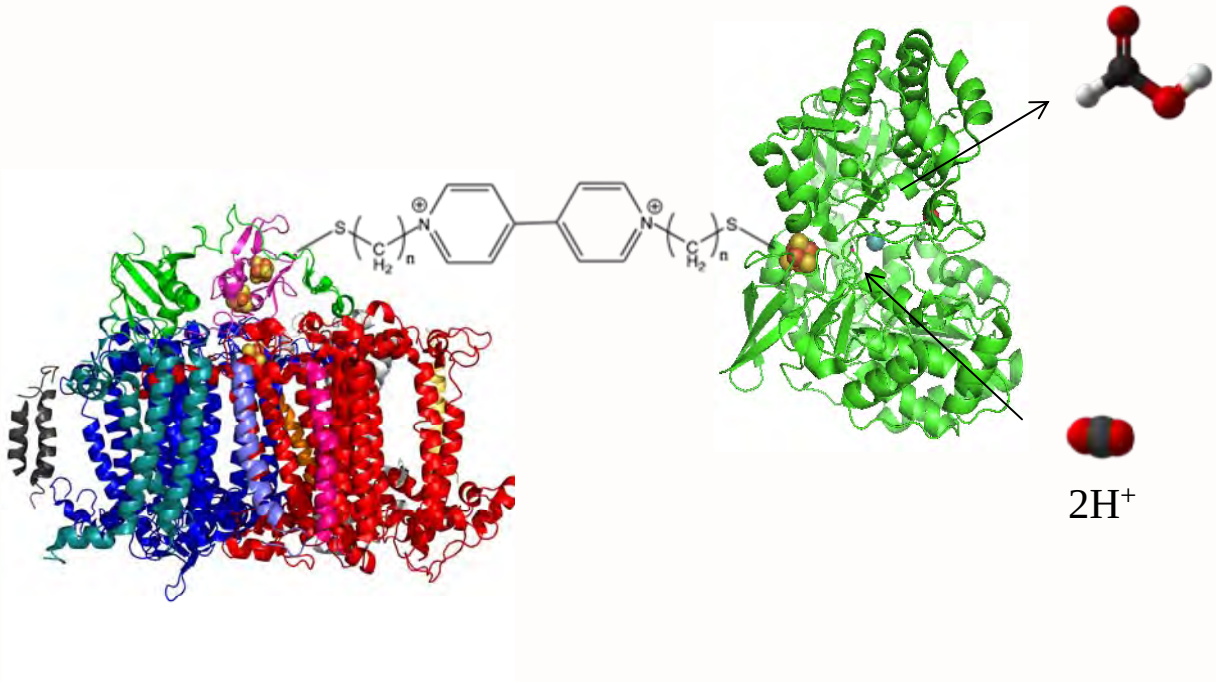
Cathodic half reaction: $2(2H^+ + 2e^- + 2h\nu \rightarrow H_2)$



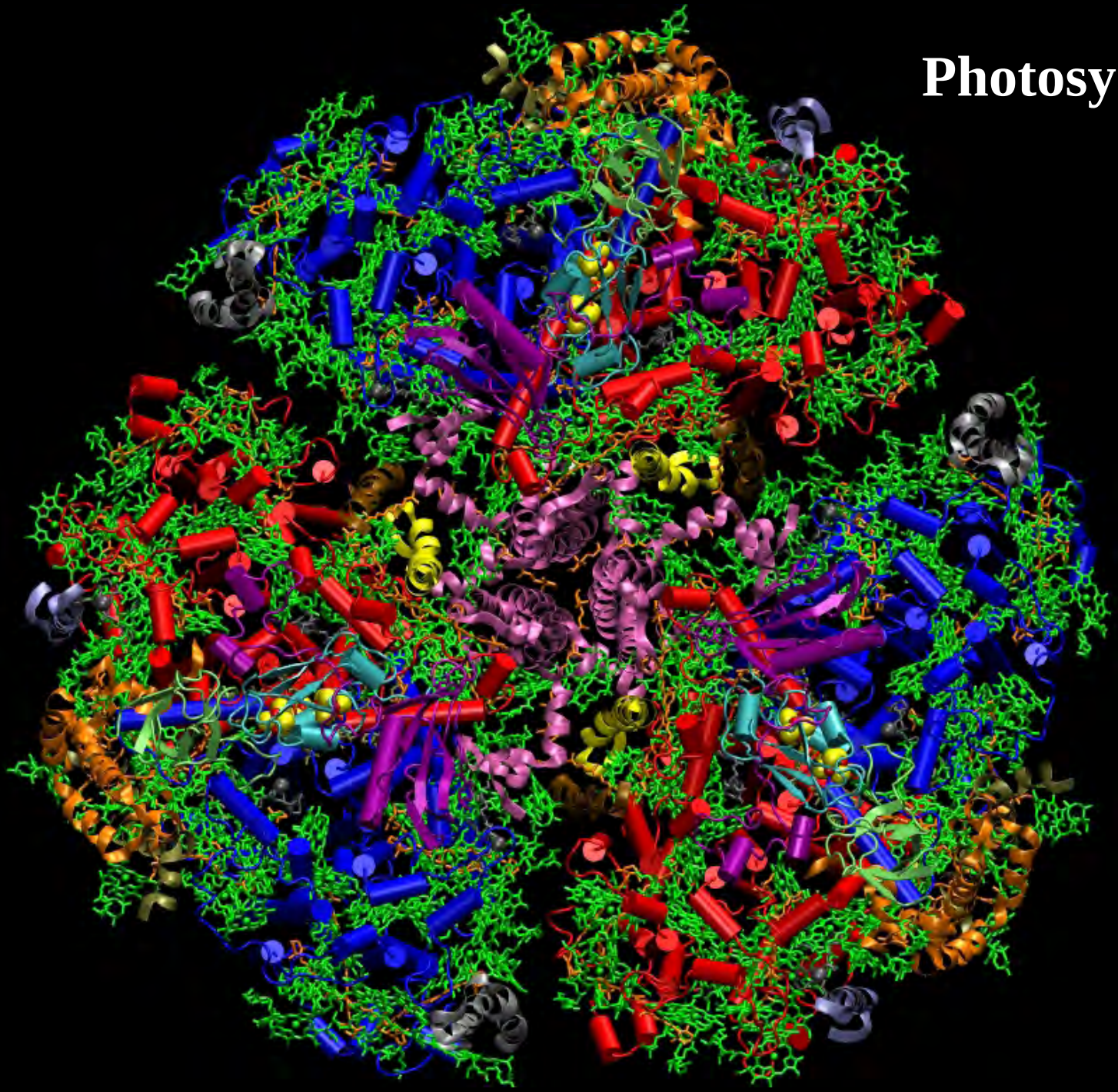
The Sensitizer: Photosystem I

The Catalyst: Formic Acid Dehydrogenase

The Coupler: A Molecular Wire

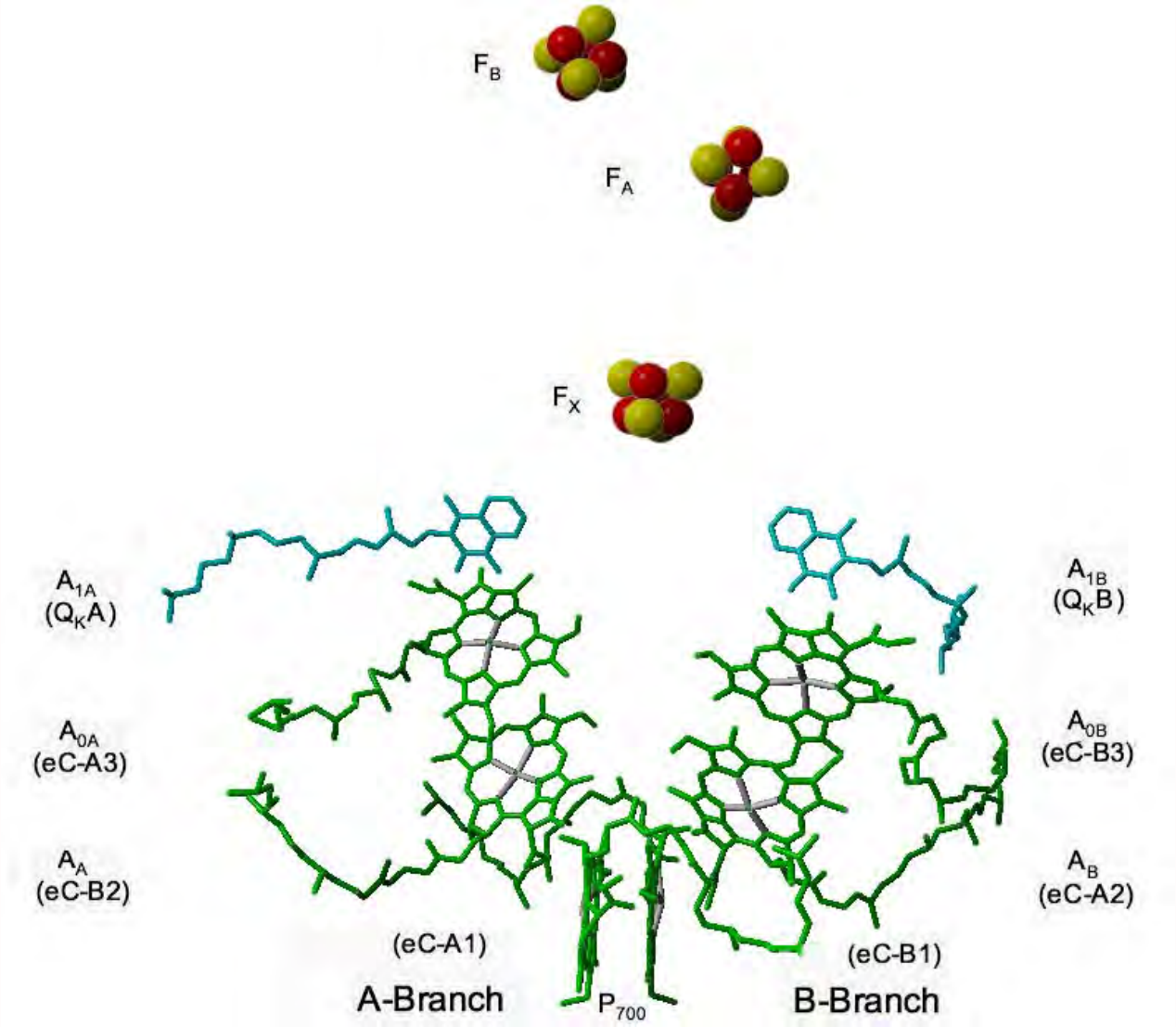


Photosystem I

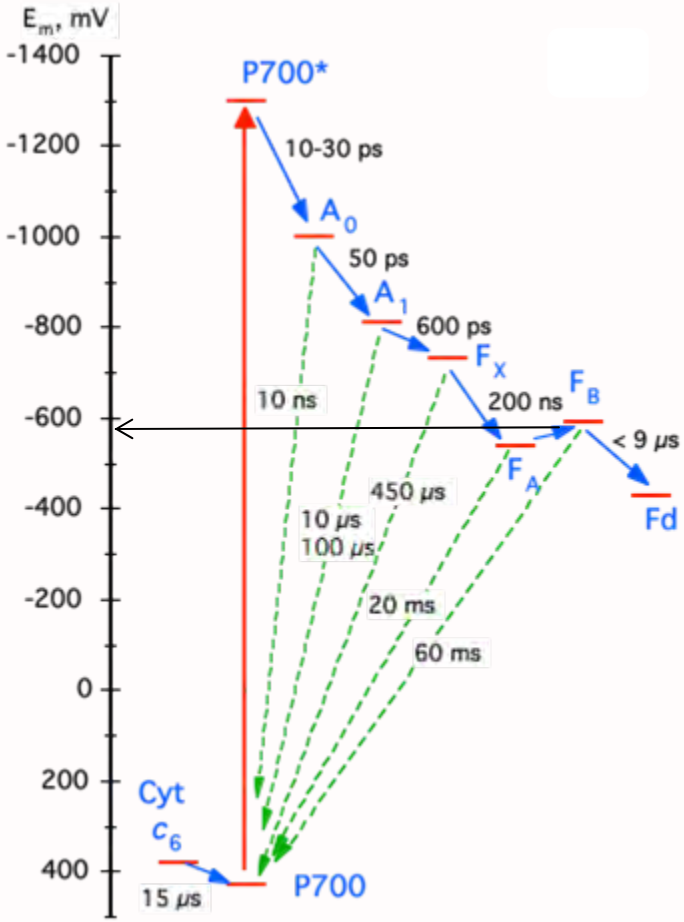


96 Chl *a*
22 β-carotene
3 [4Fe-4S]
2 Phylloquinones

Photosystem I Cofactors



Properties of Photosystem I



The F_B cluster has a pH-independent redox potential of -580 mV.

Nearly every photon that is absorbed by PS I antenna is processed into the charge separated state P_{700}^{+} F_B^{-}

The 1.01 V in the charge-separated state $P_{700}^{+}F_B^{-}$ represents a 59% conversion efficiency for a red photon, and a 38% conversion efficiency for a blue photon

The charge-separated state is stable for ~60 ms, which is sufficient time to remove the low potential electron to perform useful work

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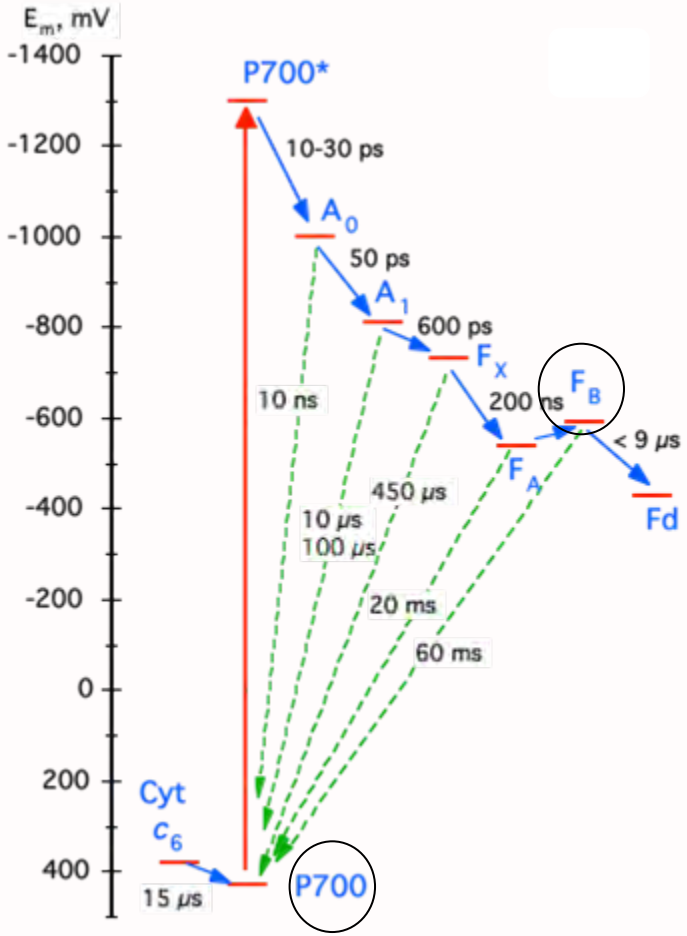

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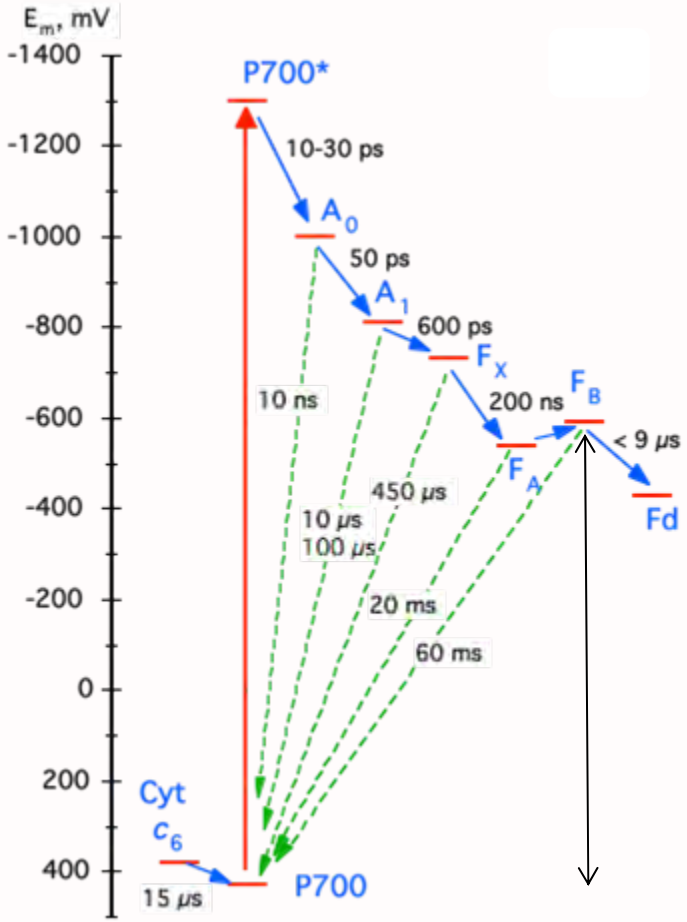

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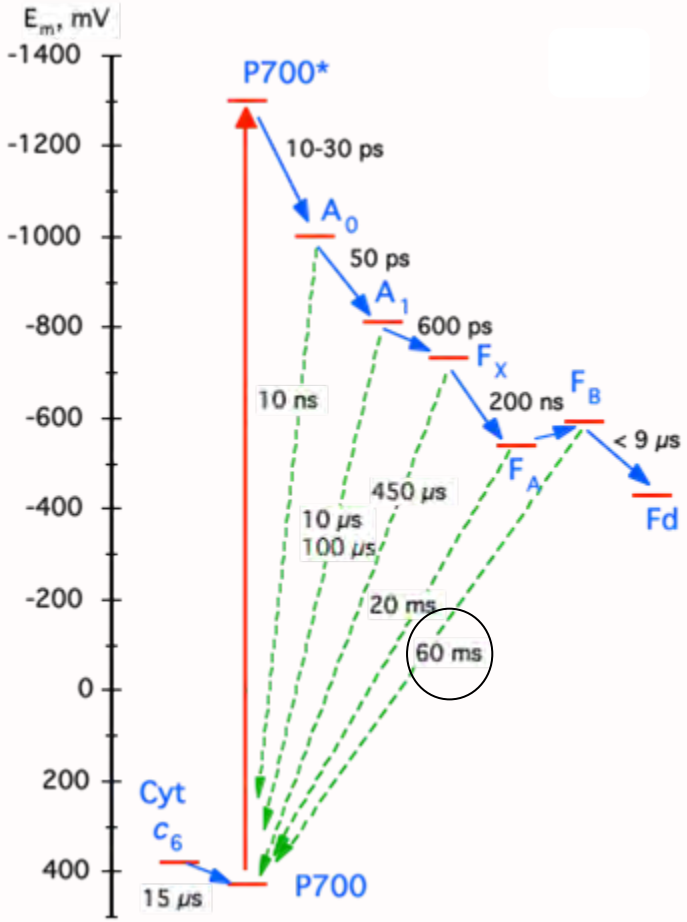

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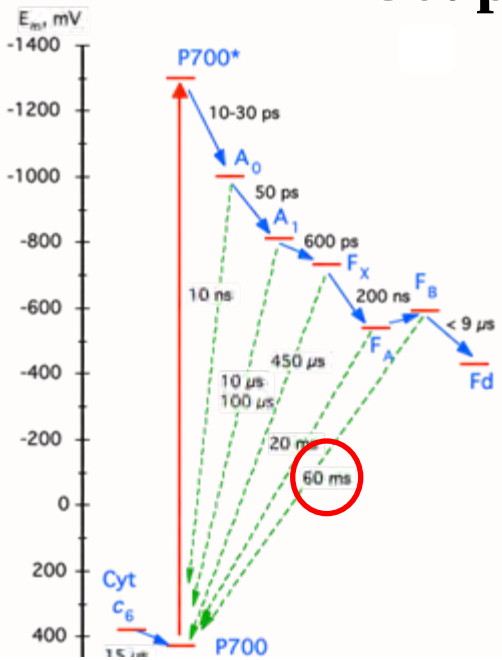
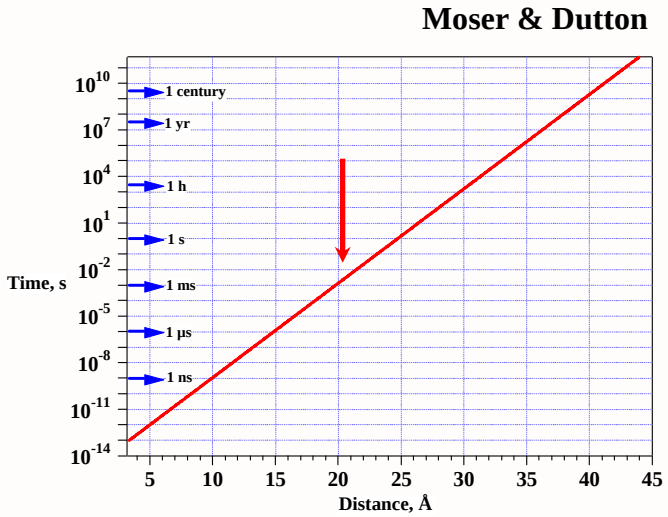
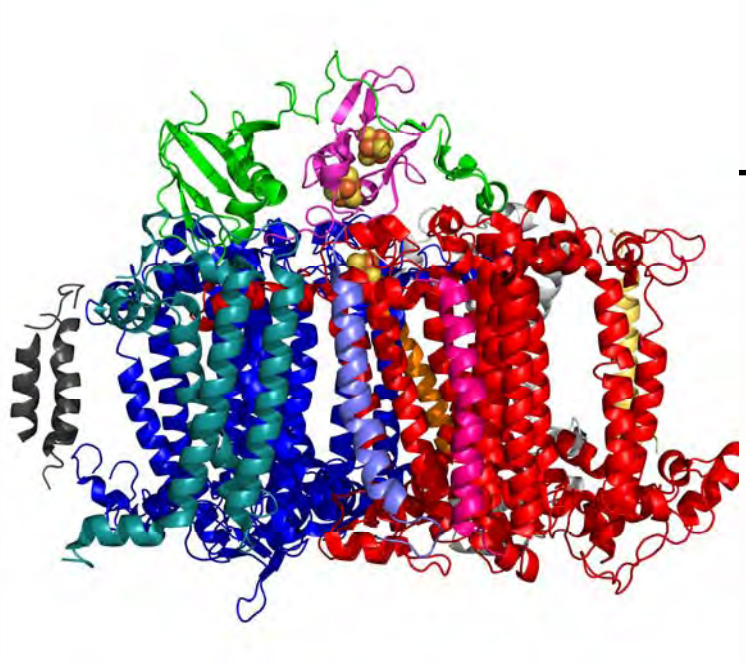
Coupling PS I to the Catalyst

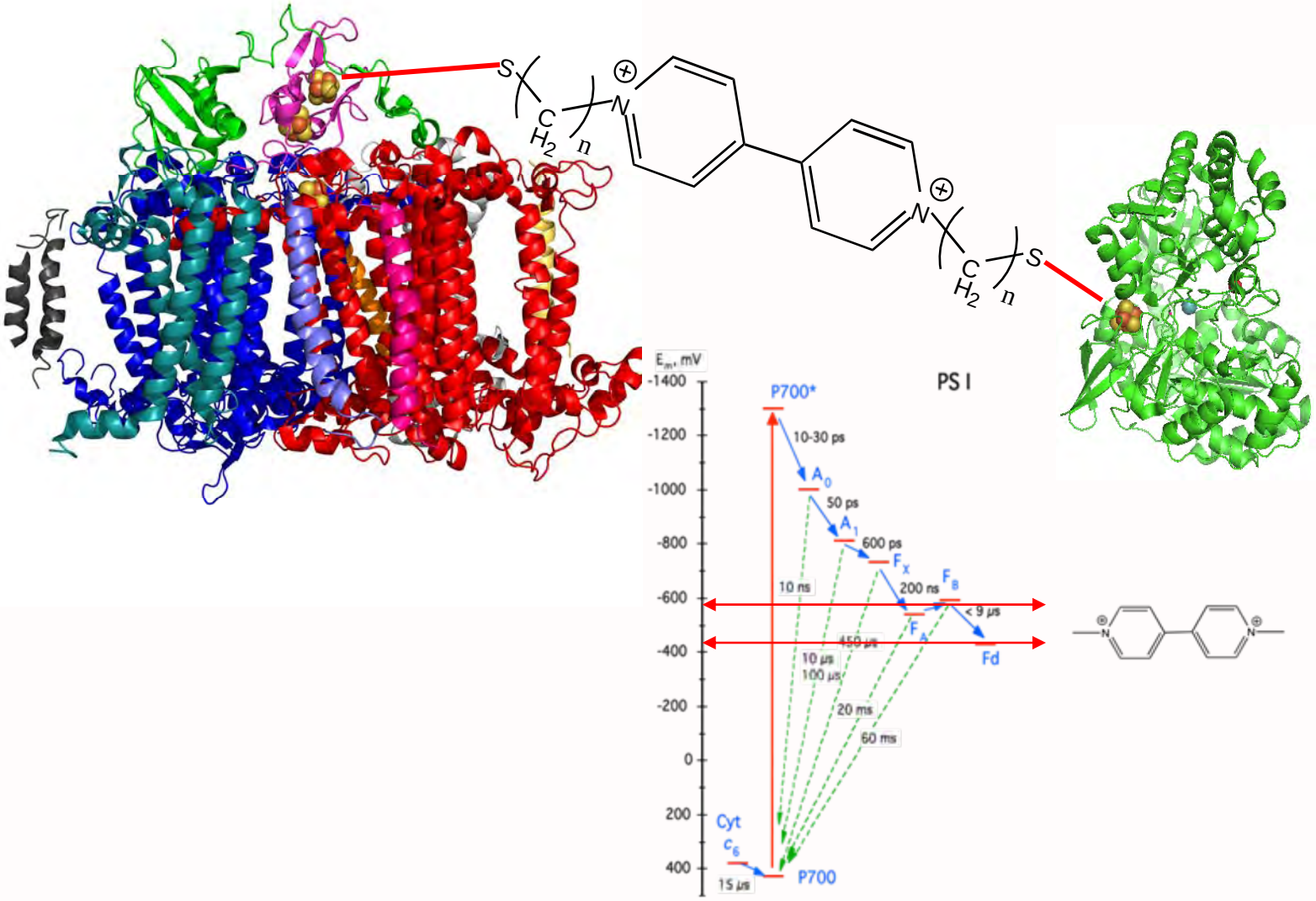






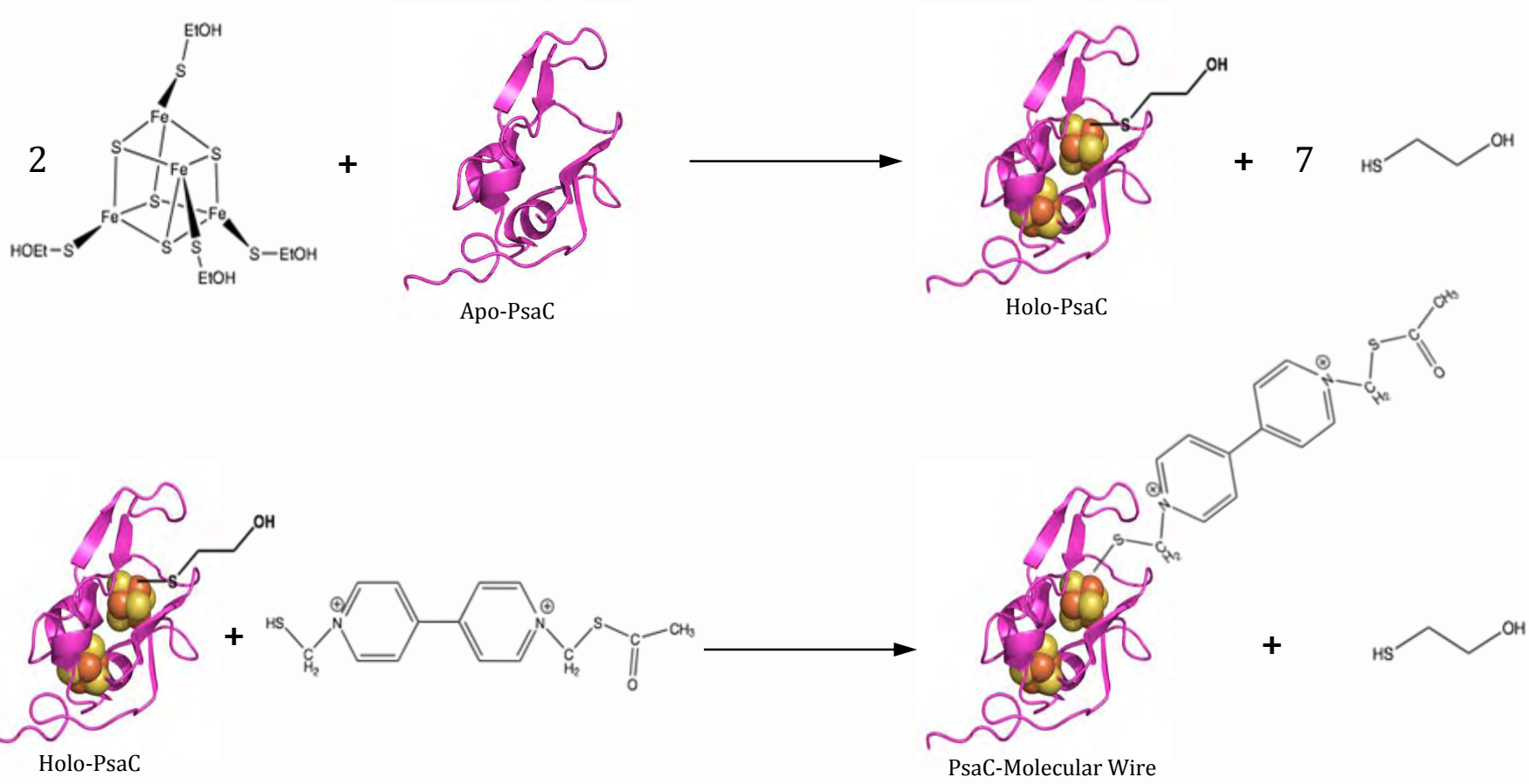
< 20 Å

Solution: Molecular Wire

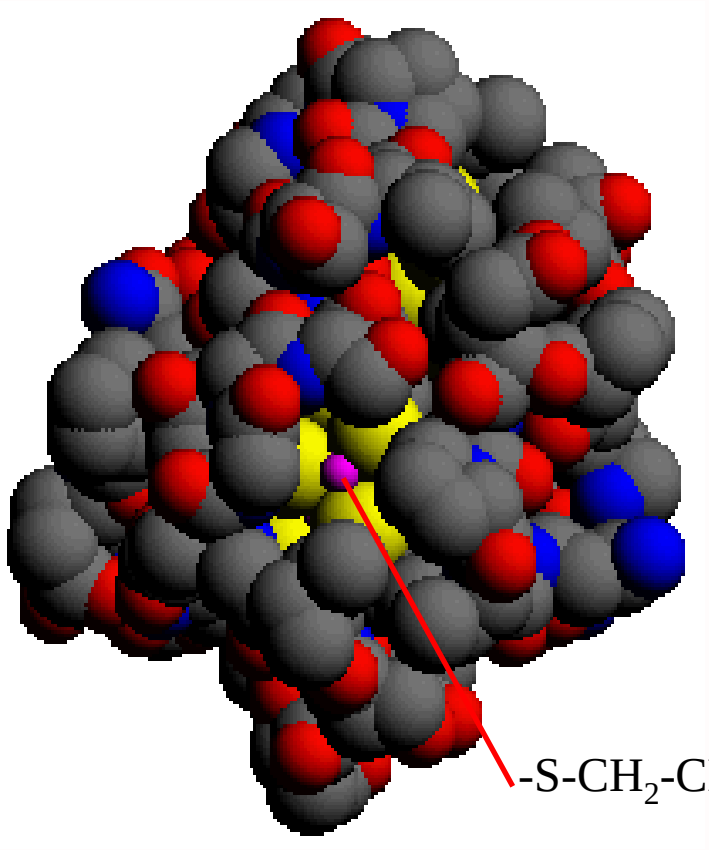


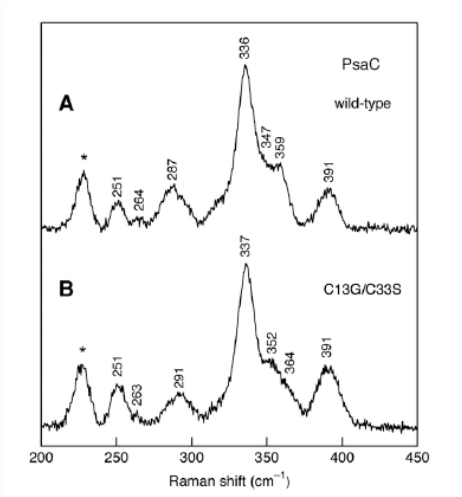
(Not to scale)

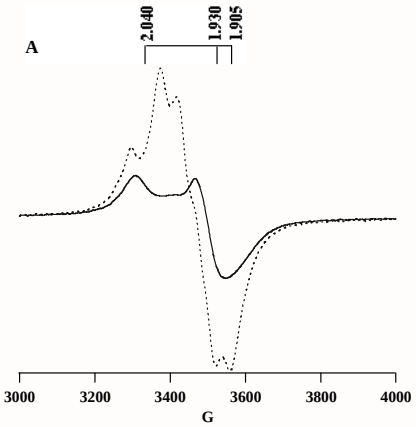
Reconstitution of Dicluster Ferredoxin

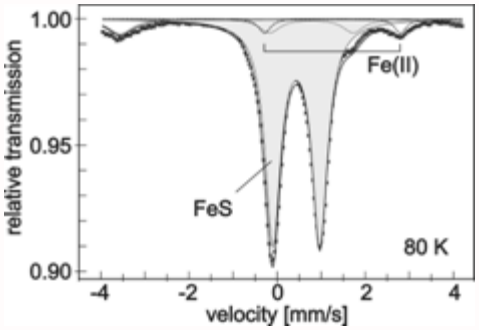


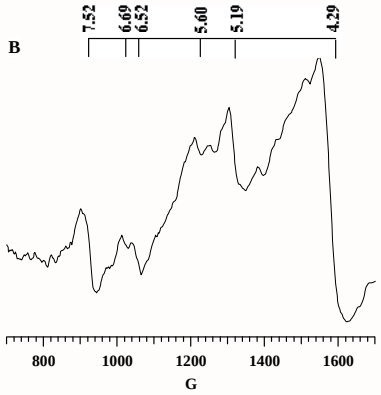
C14G Variant of PsaC





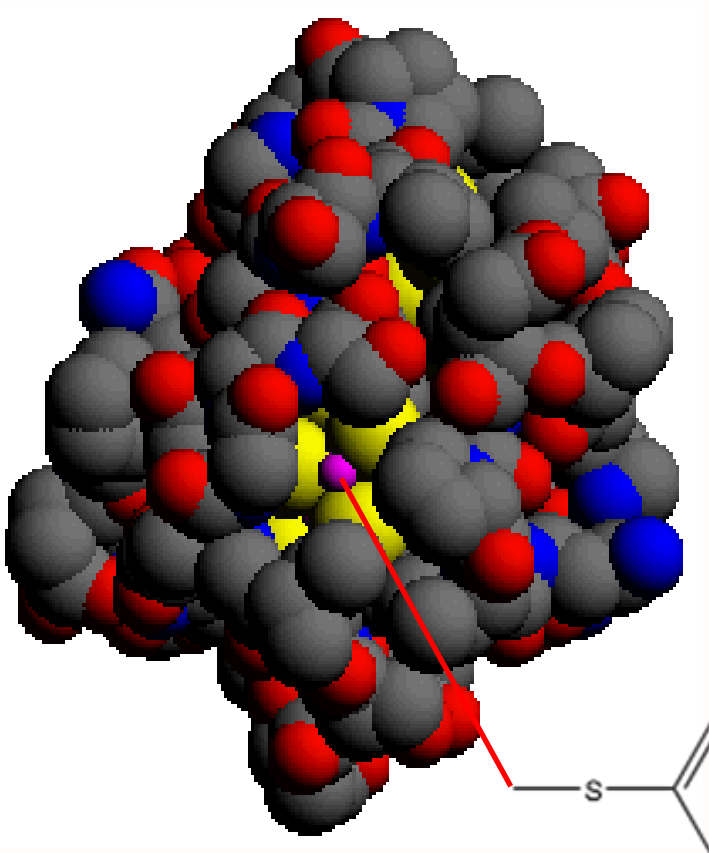




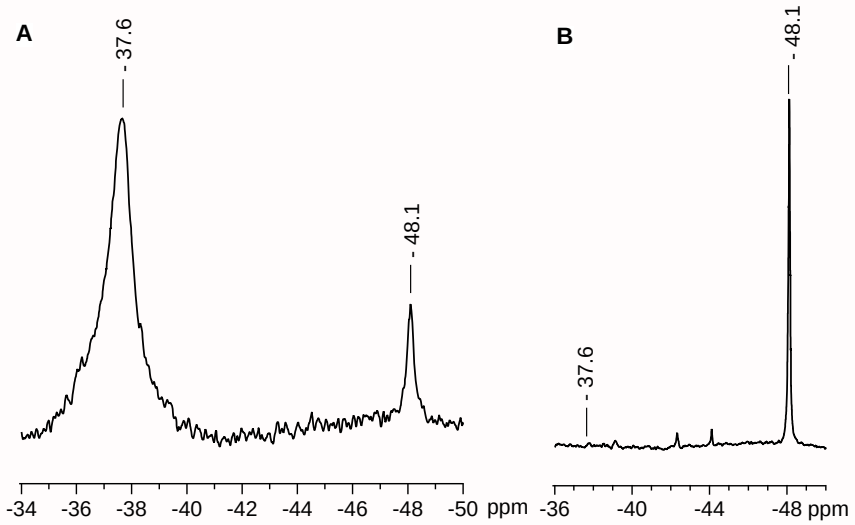


2 [4Fe-4S] **S = 1/2, 3/2**

Evidence for Rescue Ligand

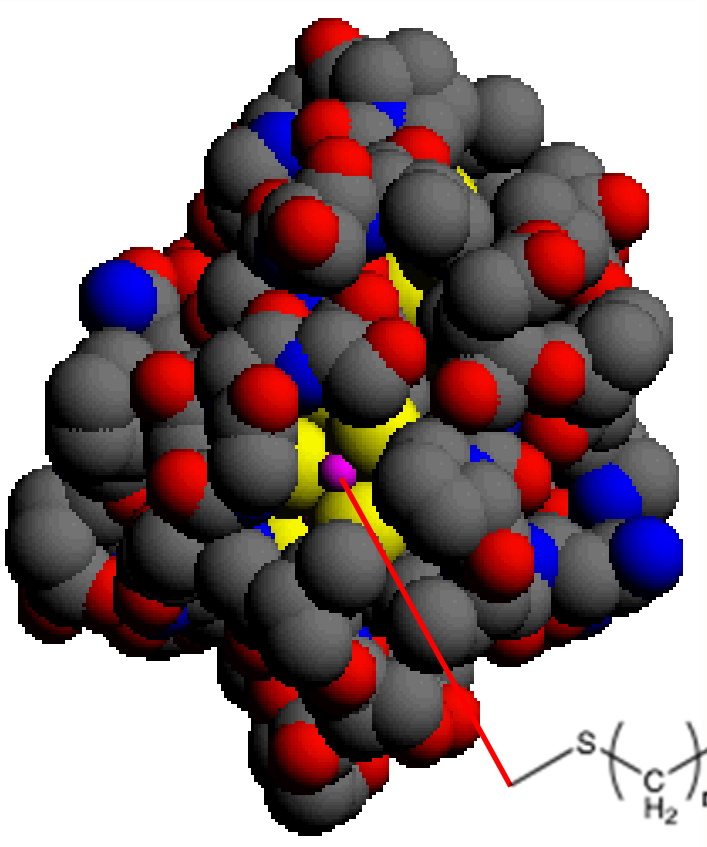


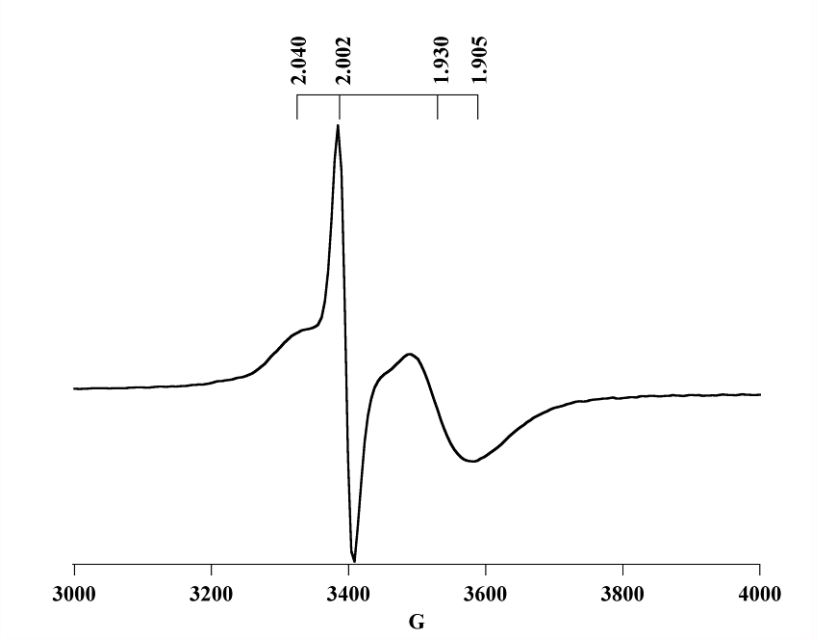
19

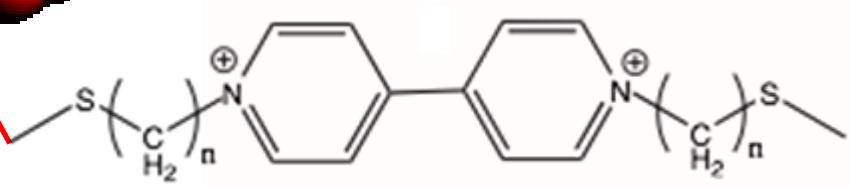


***p*-fluorothiophenol**

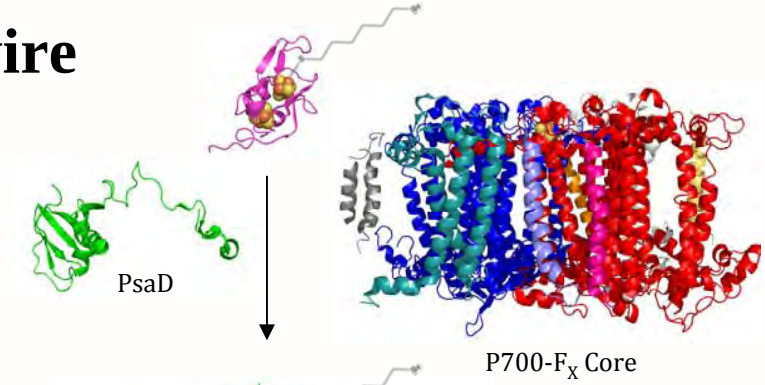
Tether Substituted 4,4’-Dipyridinium



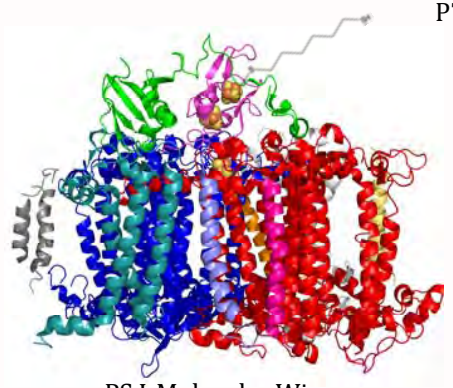




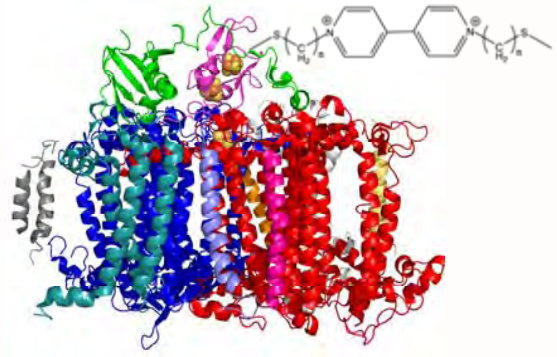
Construct PS I-wire



P700-F_X Core



PS I-Molecular Wire



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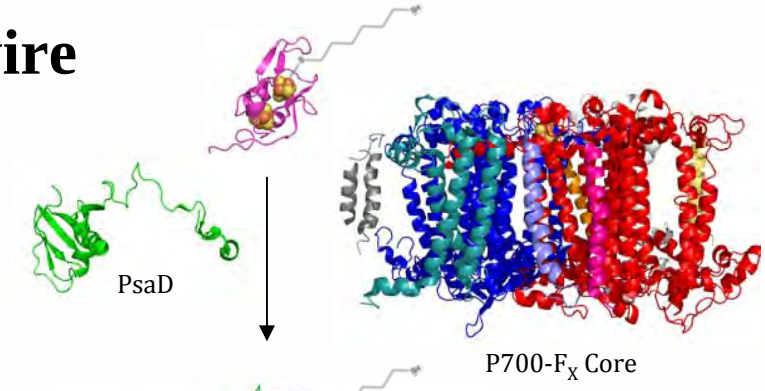

P700-F_X Core

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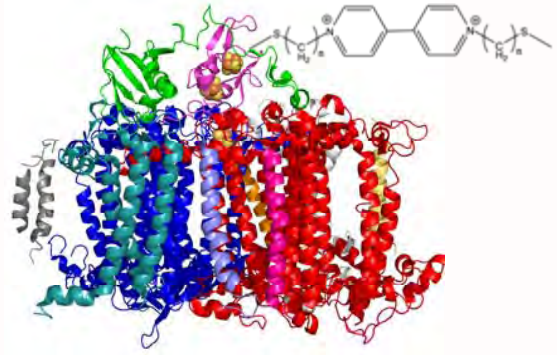
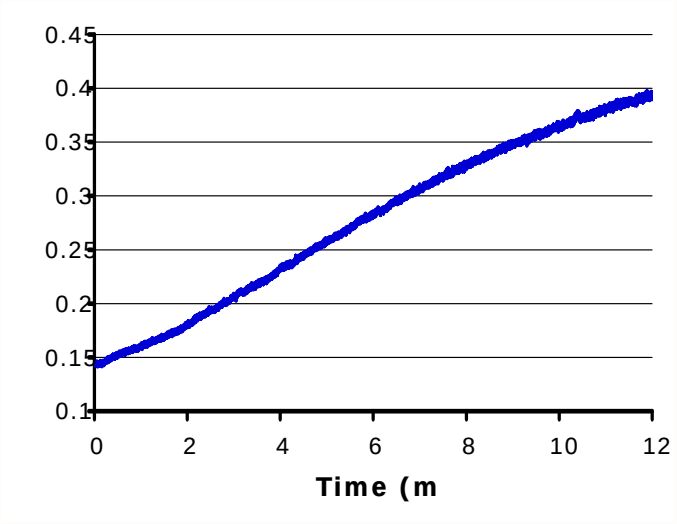
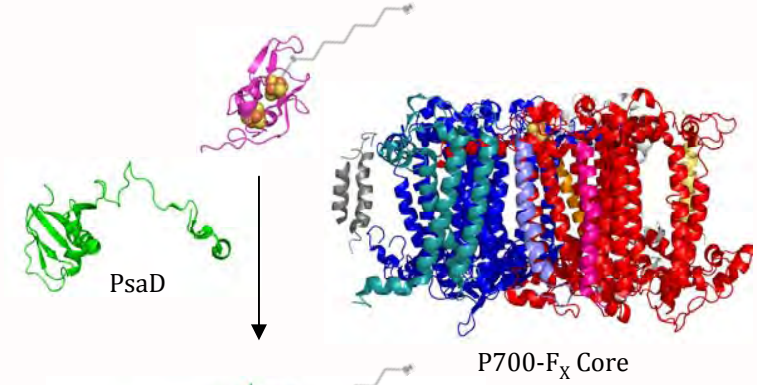
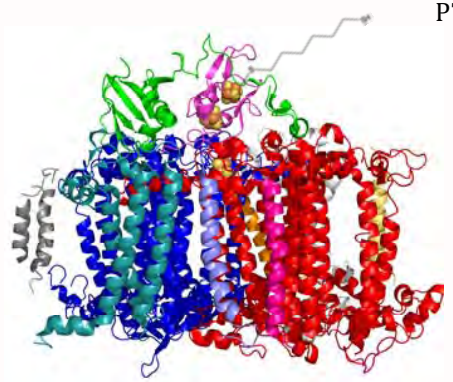


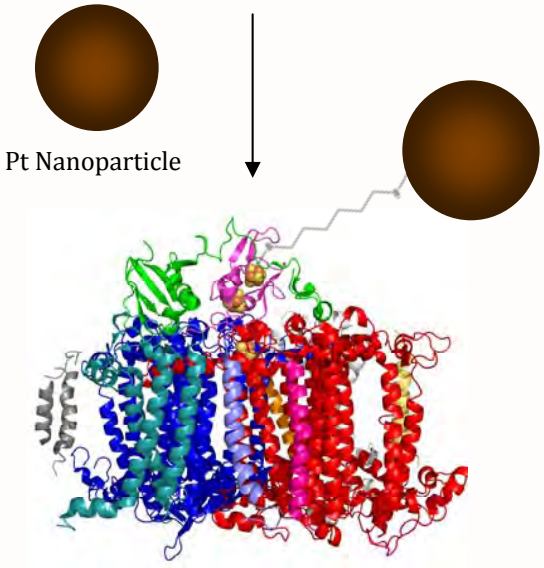


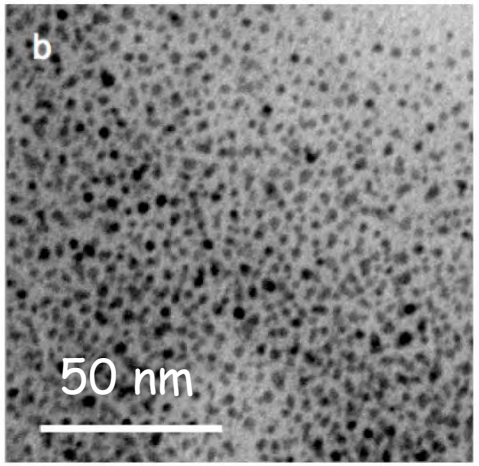
PS I-wire-Pt



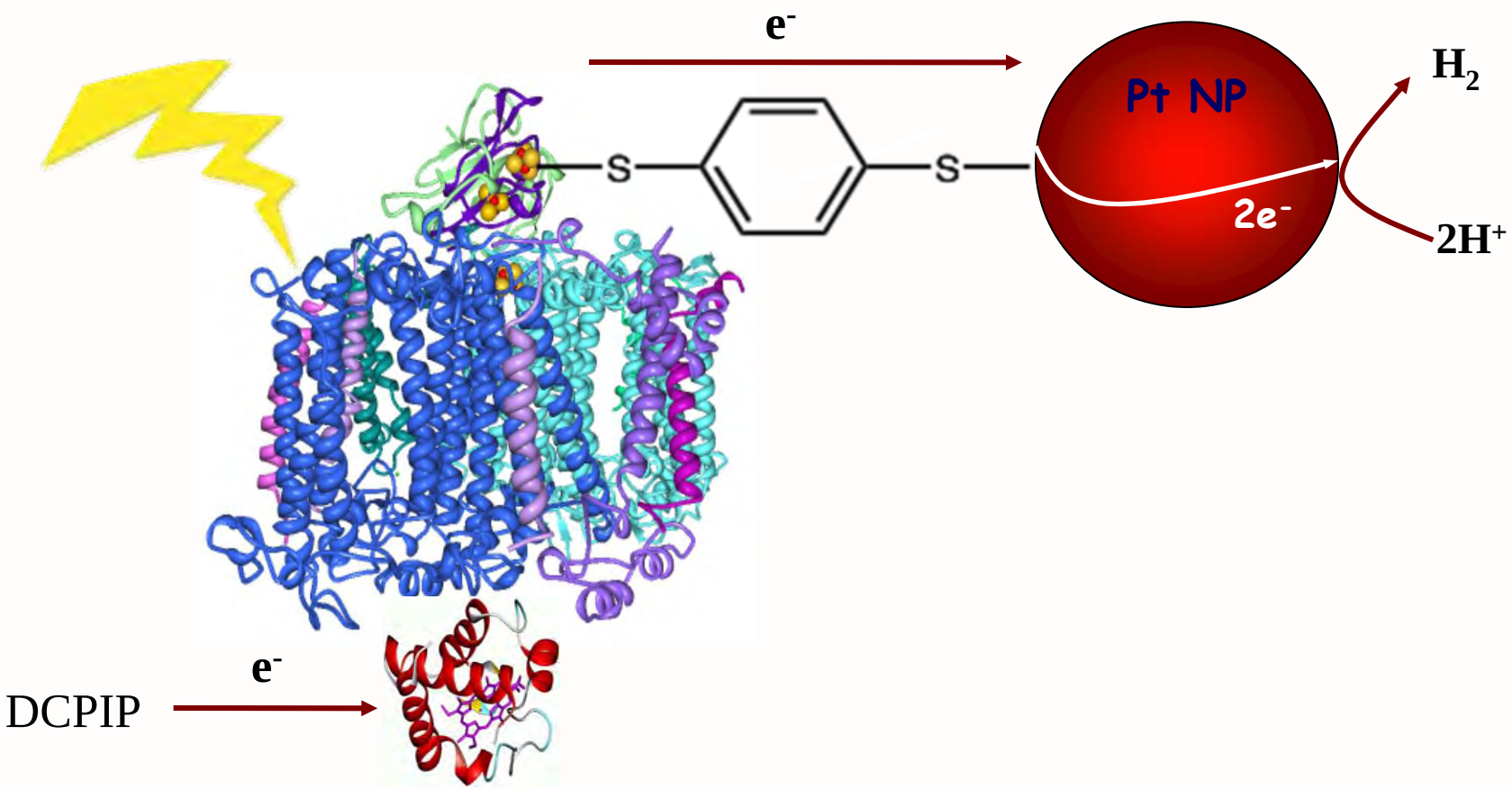


PS I-Molecular Wire



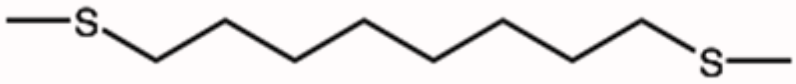
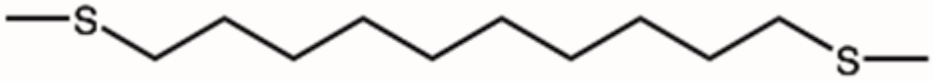
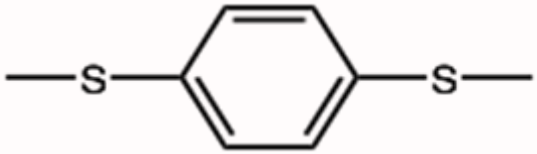


Light-Induced H_2 Production

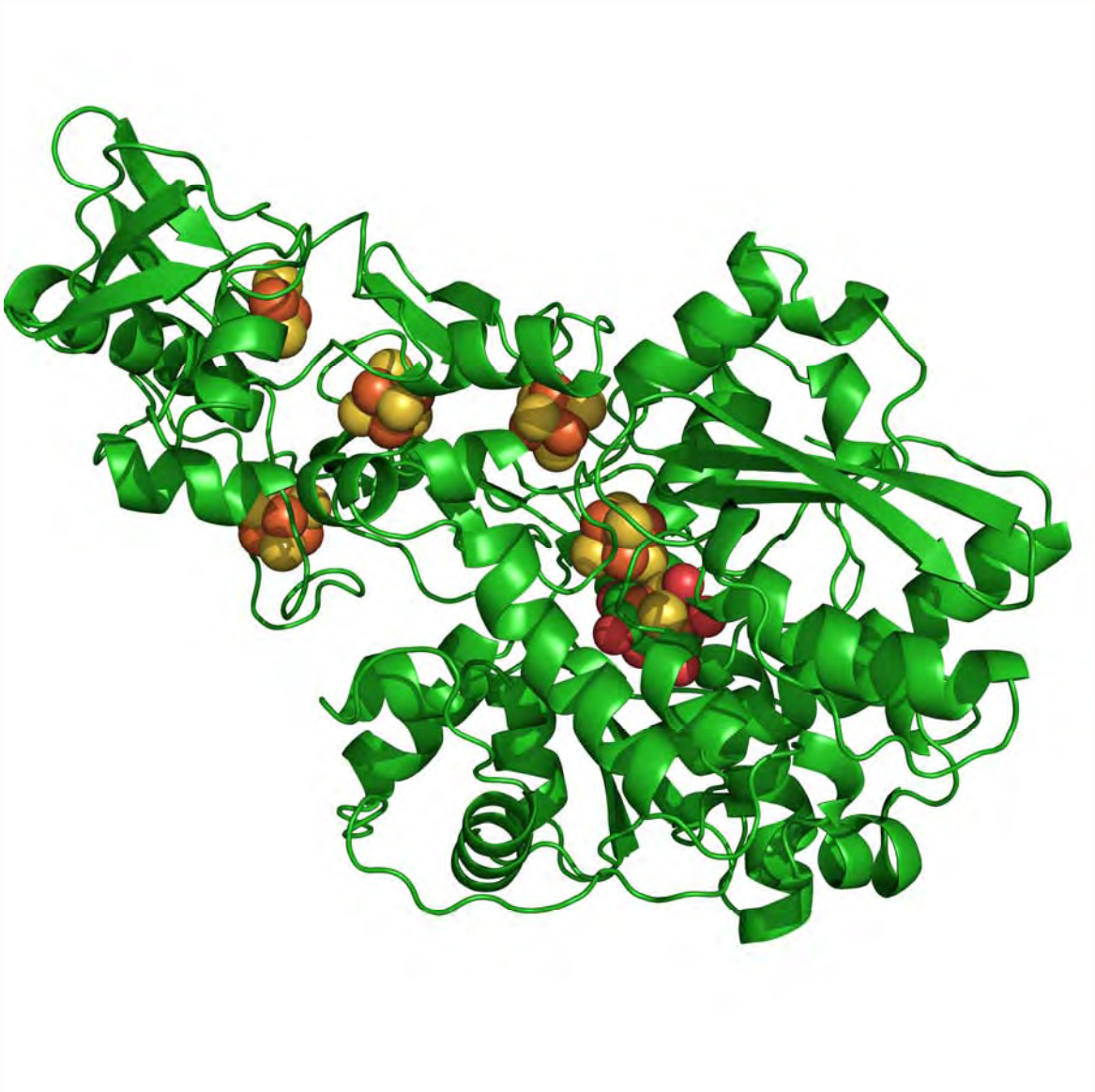


Rate = 377 μmol H_2 mg Chl^{-1} h^{-1}

Length and Identity of the Molecular Wire

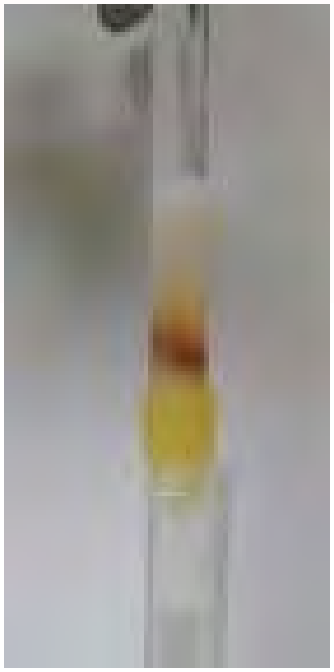
Tether	H_2 evolution rate (μmol H_2 mg Chl^{-1} h^{-1})
 1,3-propanedithiol	2.2
 1,6-hexanedithiol	57.7
 1,8-octanedithiol	40.8
 1,10-decanedithiol	13.6
 1,4-benzenedithiol	159.4

Desulfovibrio desulfuricans Fe-Fe H_2ase



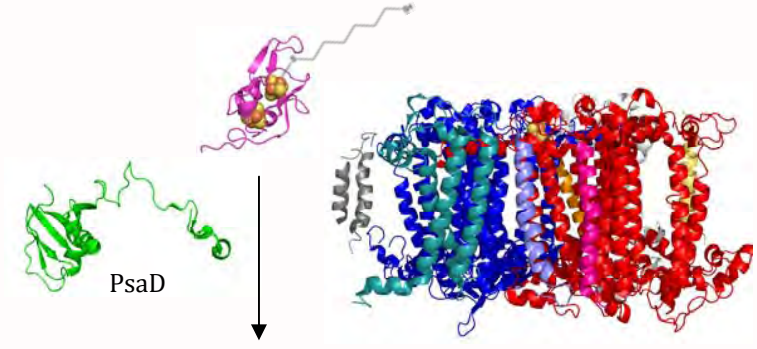
Purification of HydA and Cys_{98}->Gly Mutant

HydA



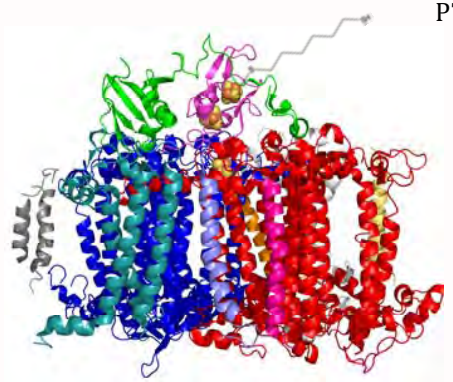
Cys_{98}->Gly Mutant

PS I-wire-H_2ase

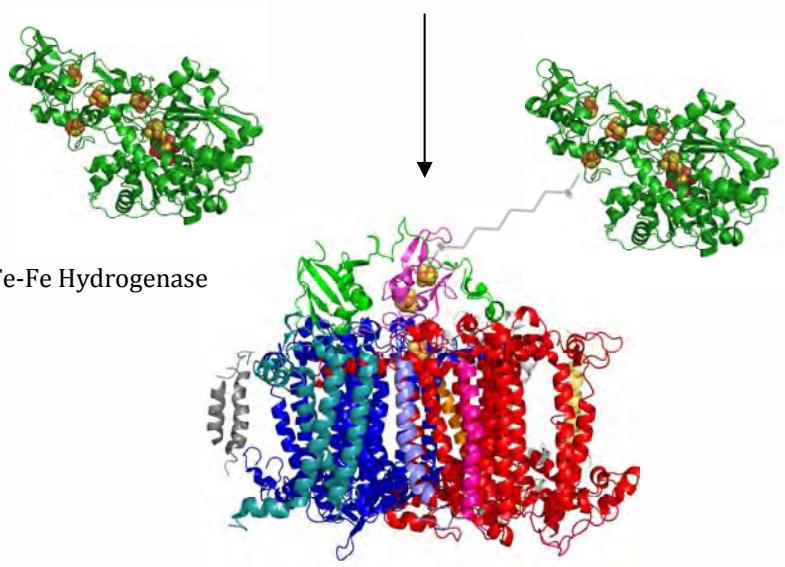


PsaD

P700-F_X Core

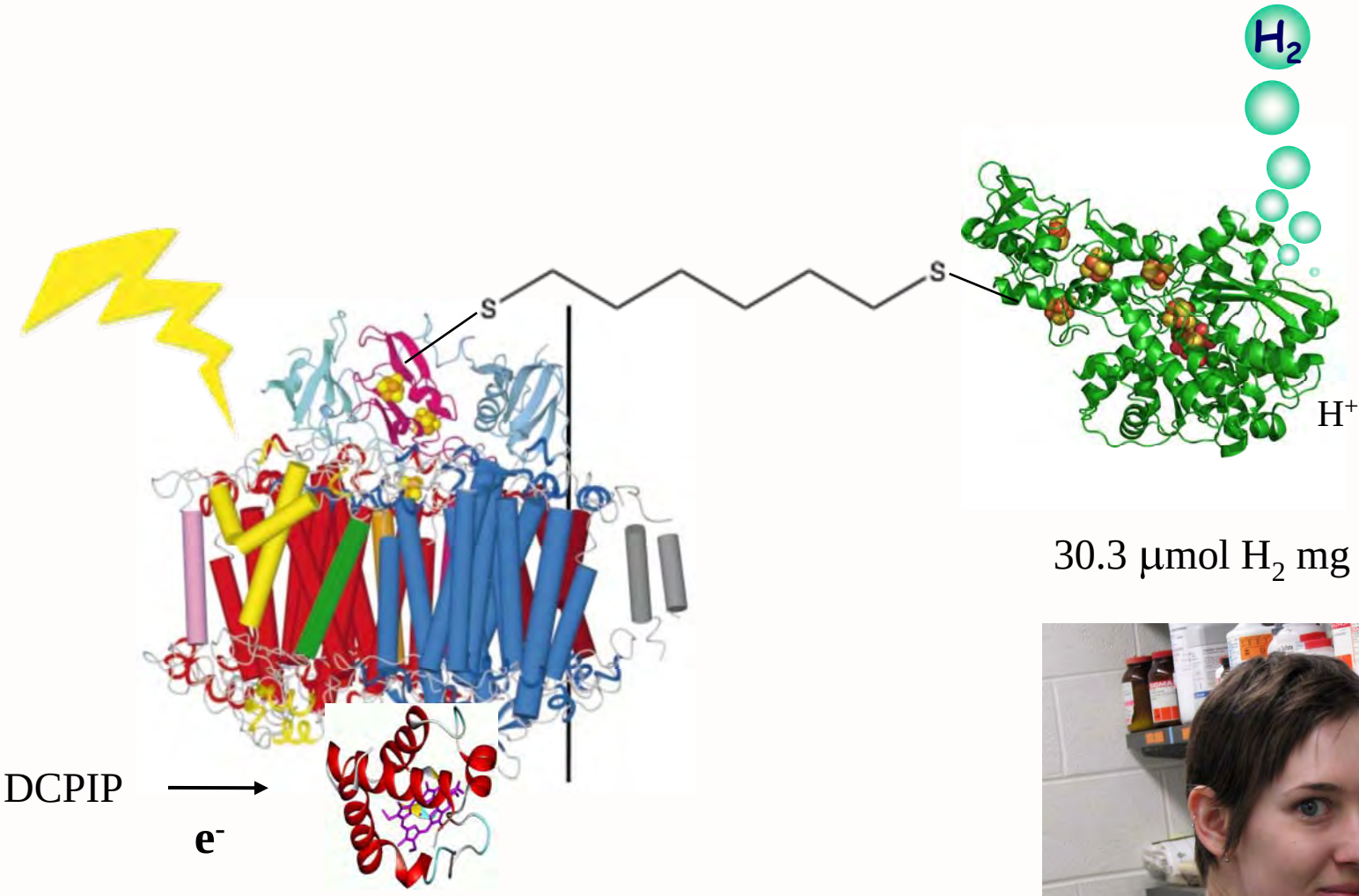


PS I-Molecular Wire



Mutant Fe-Fe Hydrogenase

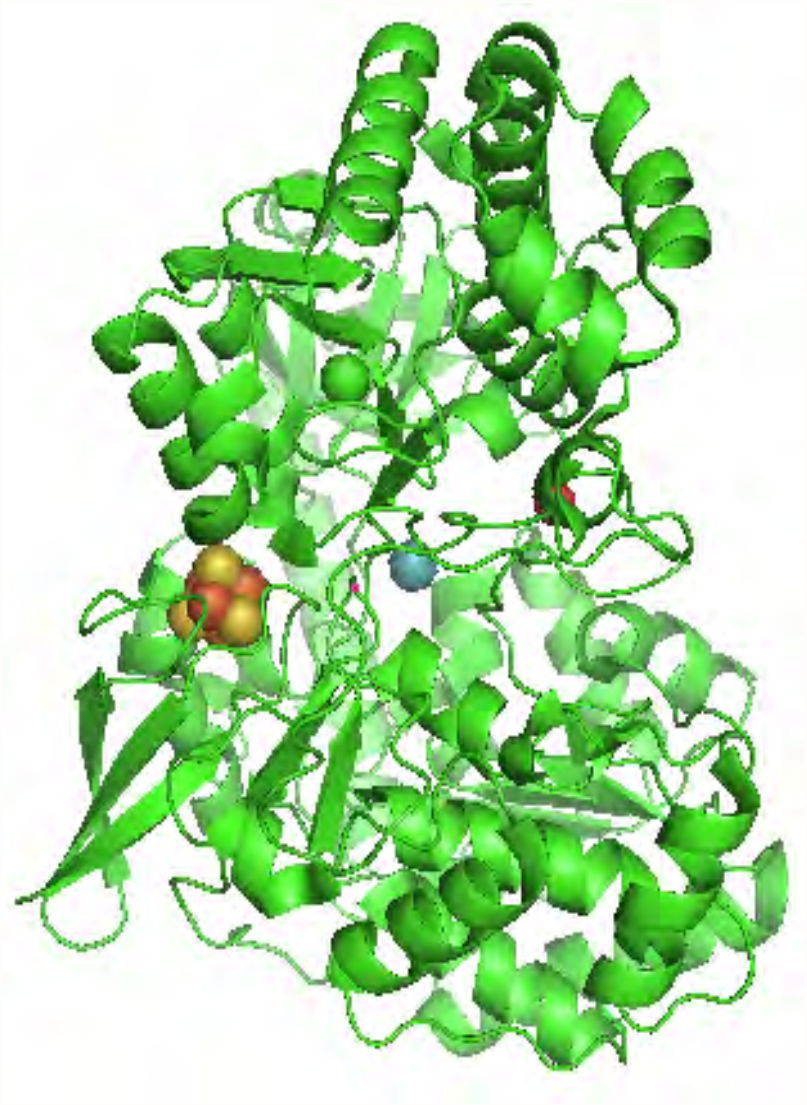
PS I-Molecular Wire-H_2ase



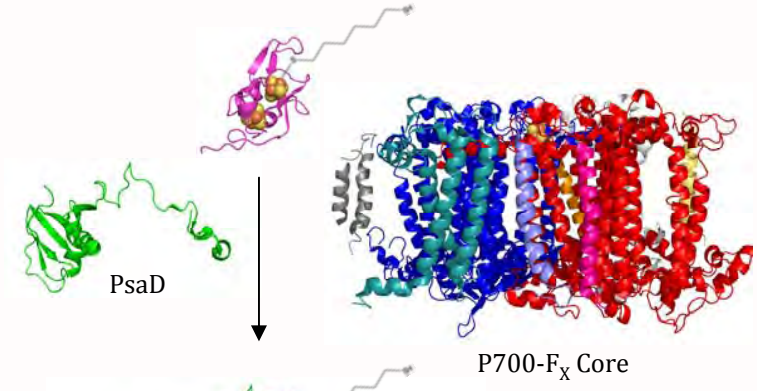
30.3 μmol H_2 mg Chl^{-1} hr^{-1}

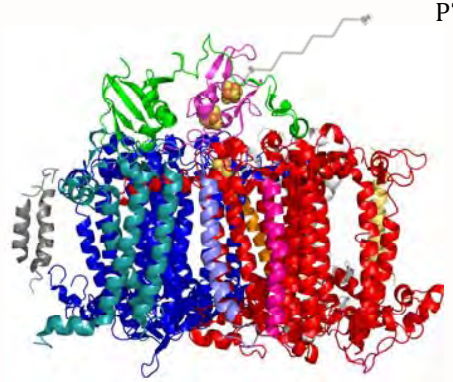
Carolyn Lubner

Escherichia coli Formate Dehydrogenase

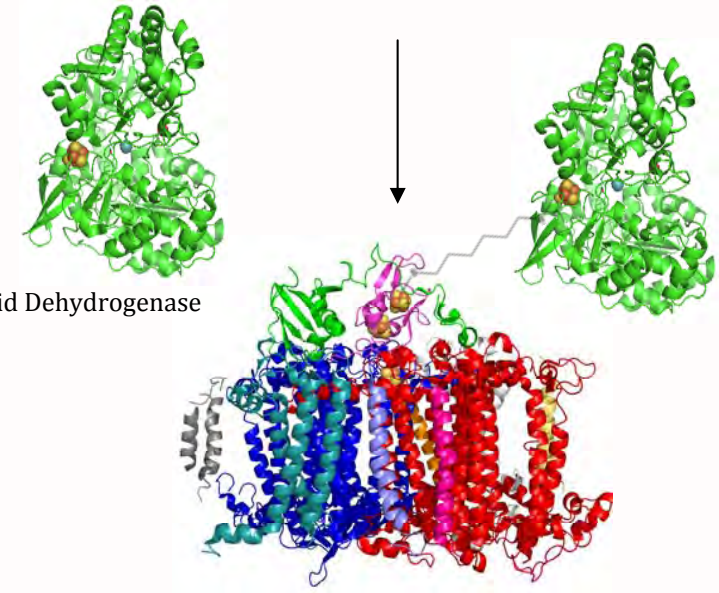


PS I-wire-FDH



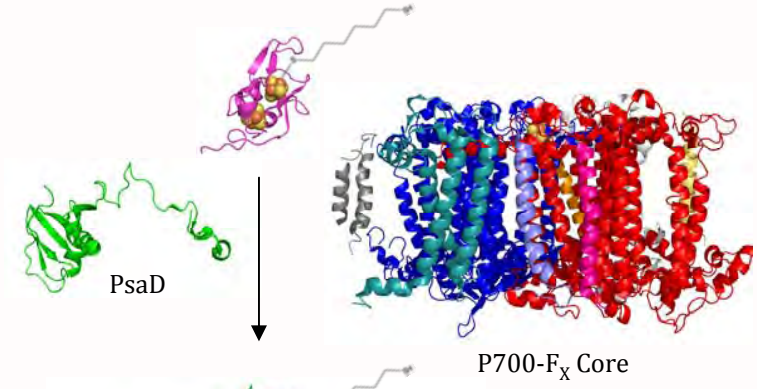


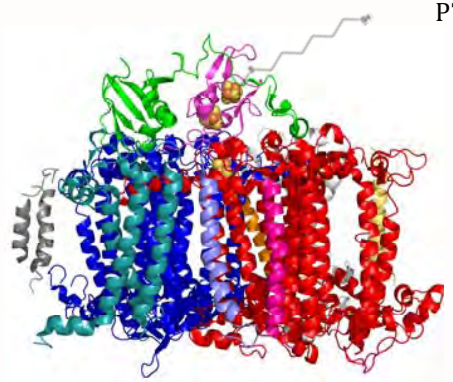
PS I-Molecular Wire



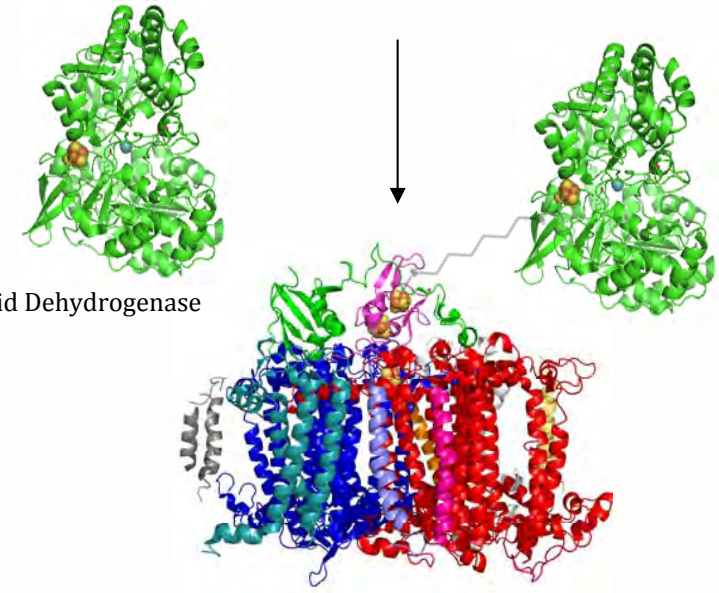
Mutant Formic Acid Dehydrogenase

PS I-wire-FDH





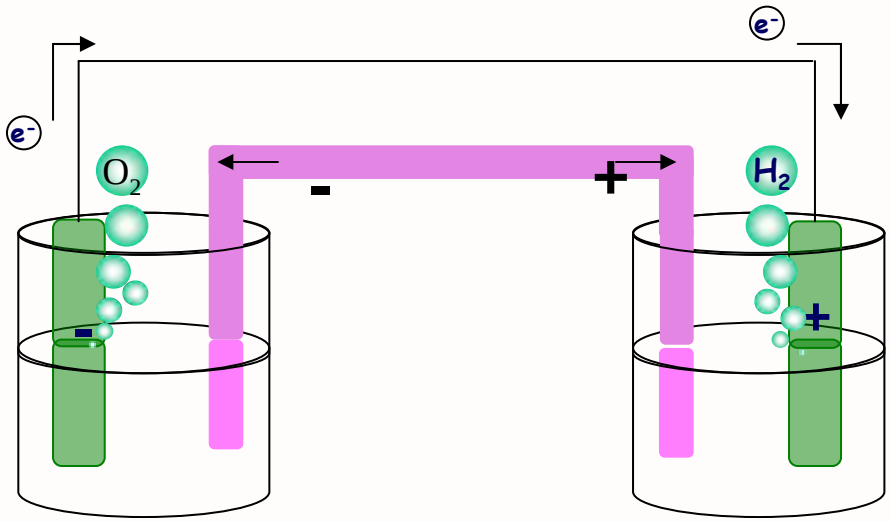
PS I-Molecular Wire



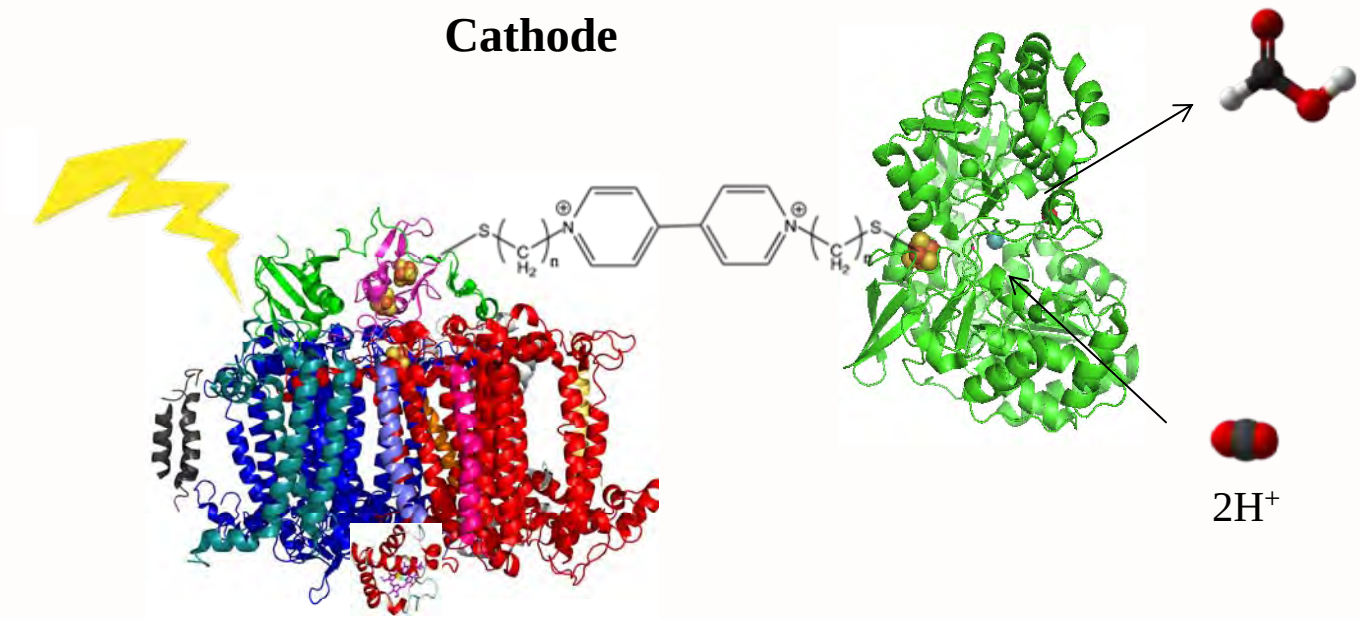
Mutant Formic Acid Dehydrogenase

In Progress

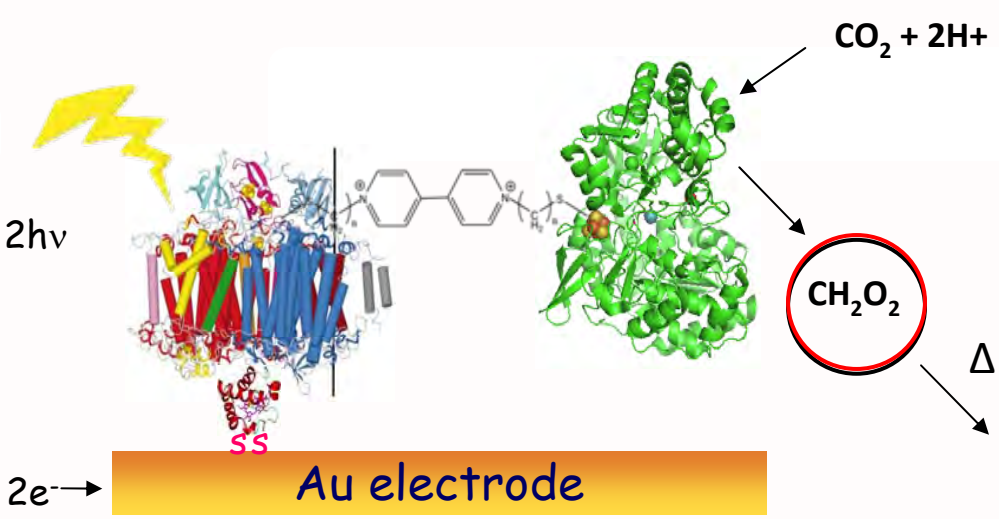
Biological/Organic Hybrid Half-Cell



Anode **Cathode**

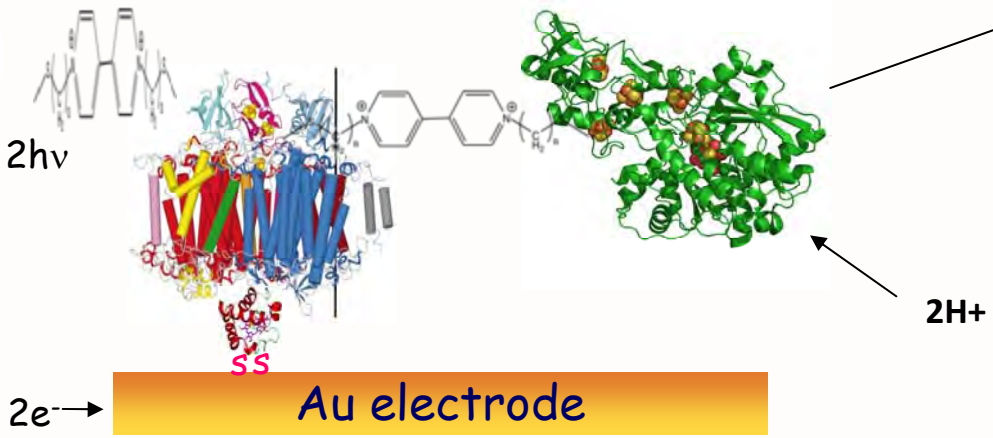


High Density Liquid Fuel



$CO + H_2O$

$(2n+1)\ H_2 + n\ CO \rightarrow C_nH_{(2n+2)} + n\ H_2O$

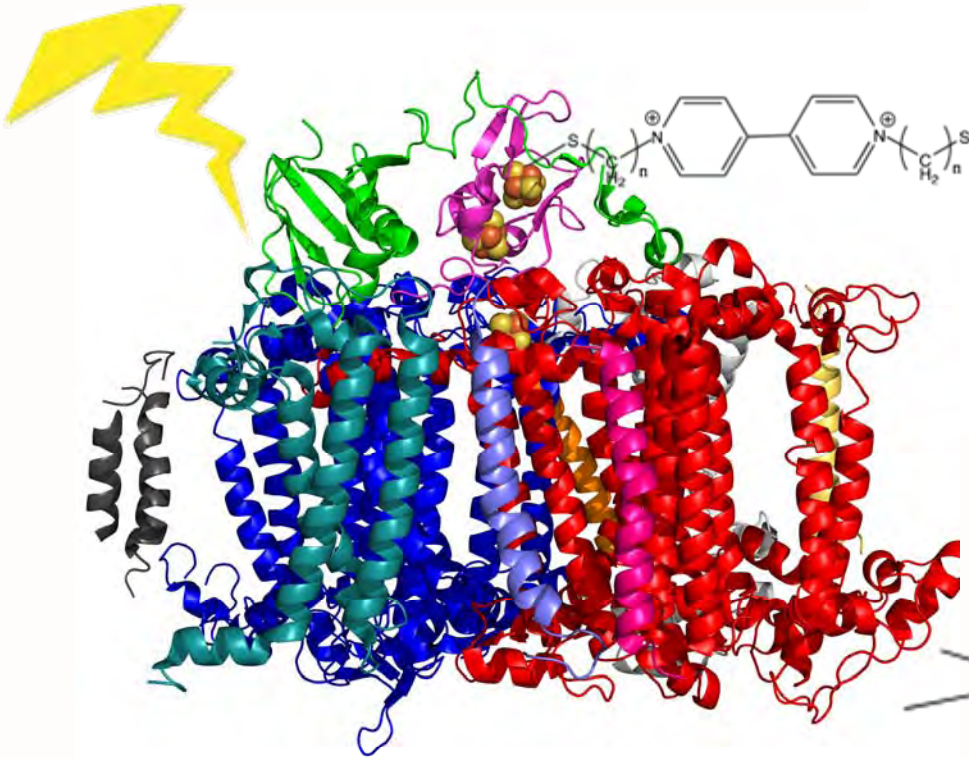


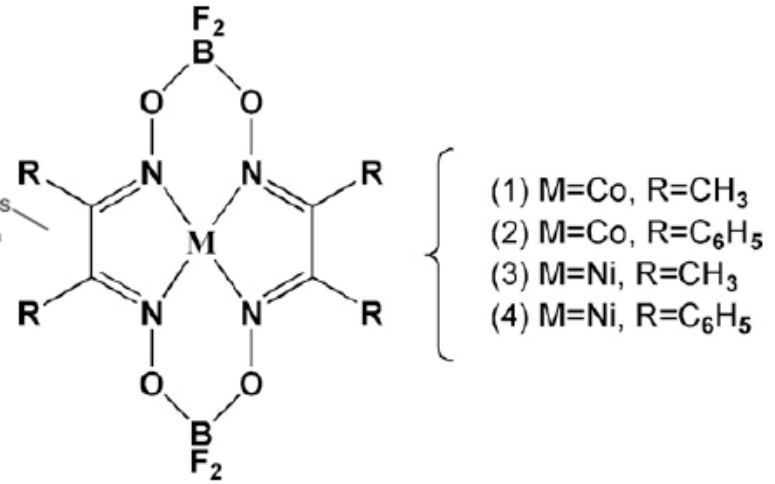
Fischer-Tropsch

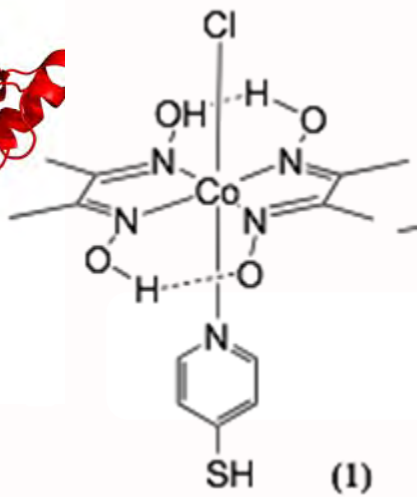
Water Gas Shift

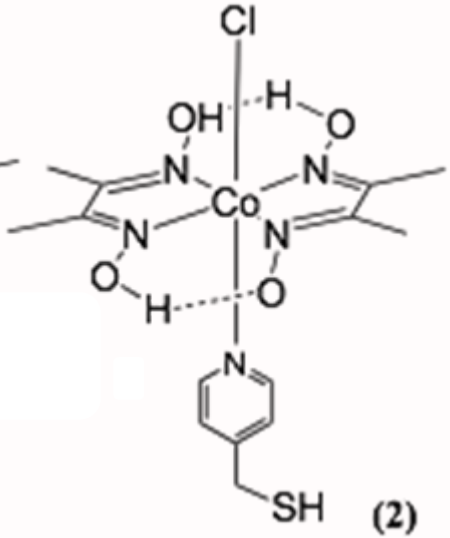
$CO_2 + H_2 \leftrightarrow CO + H_2O$

Cobalt Difluoroboryl Diglyoximate Catalyst









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