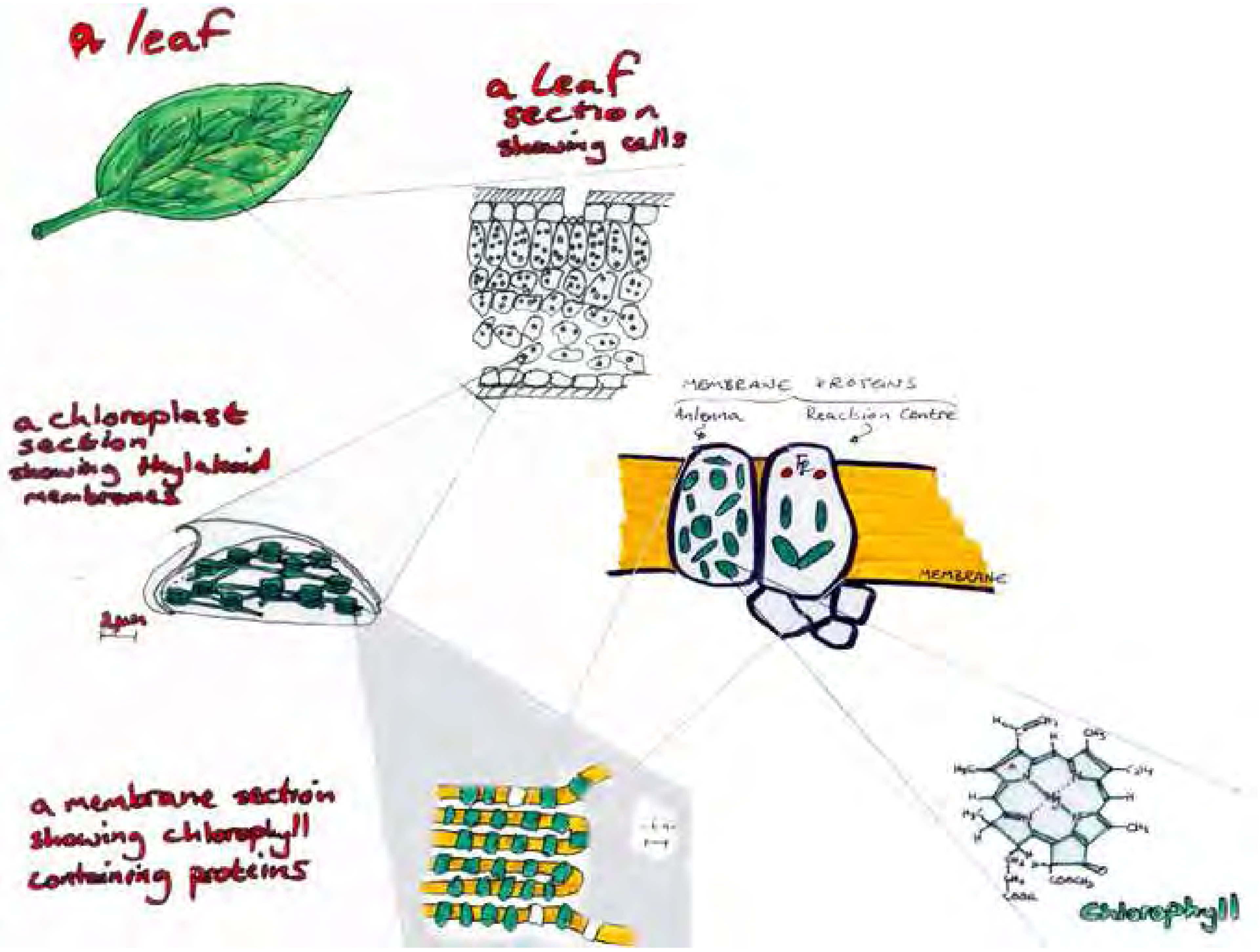
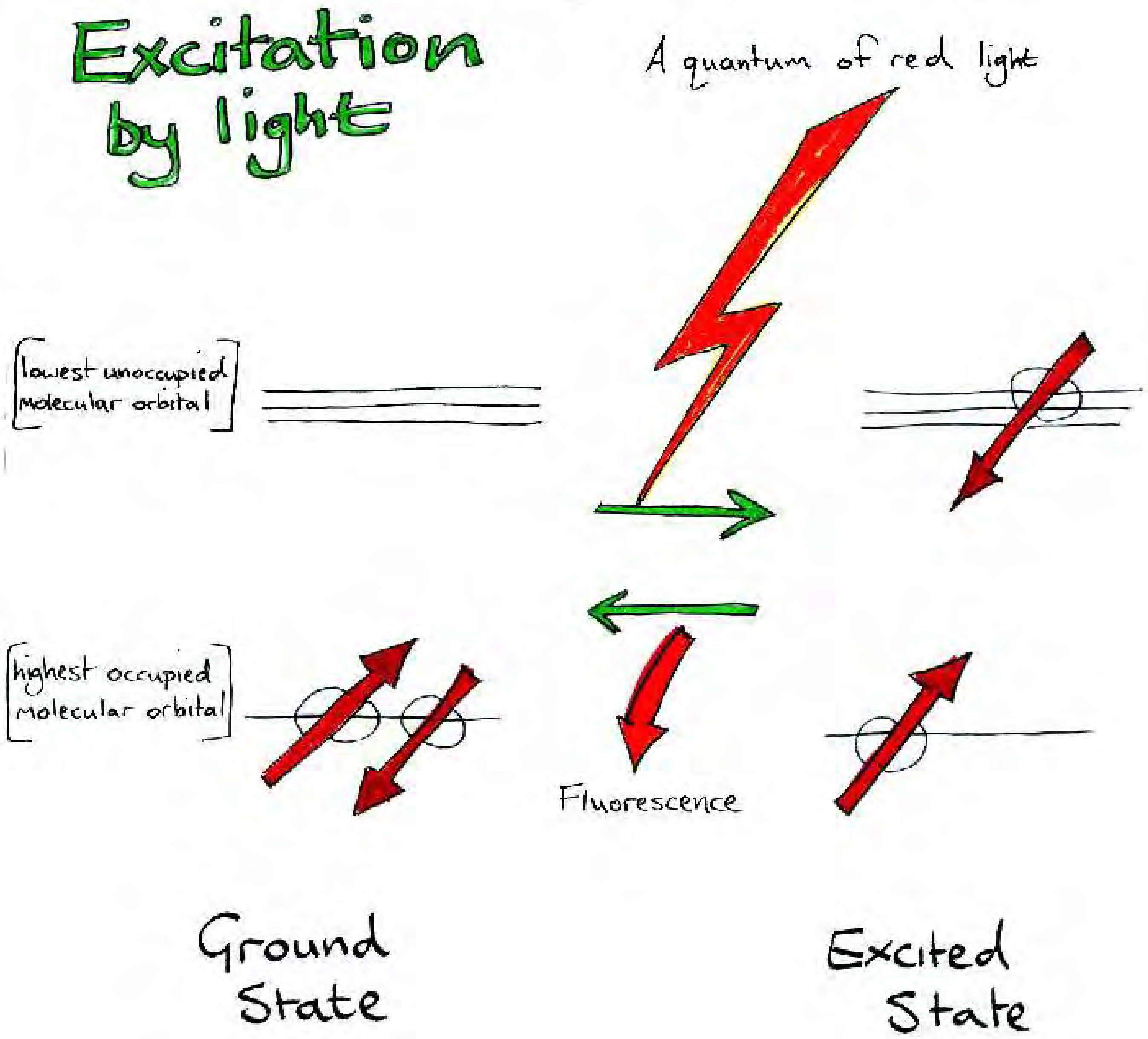
The O_2 evolving enzyme

A.W. RUTHERFORD

ref: - Goussias, Boussac & Rutherford 2002
Philosophical Trans. 357, 1369-1381

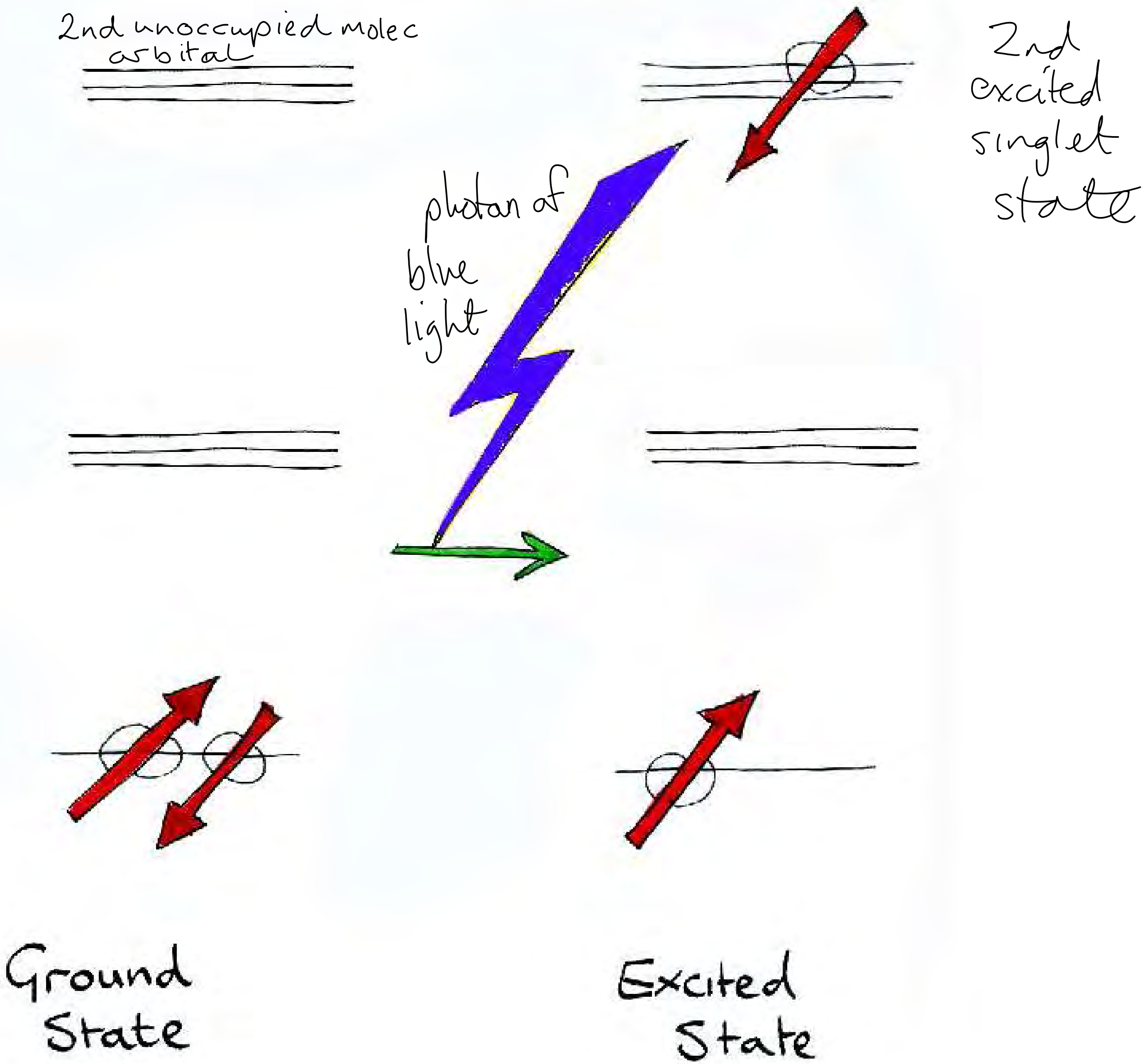
- Rutherford & Boussac 2004 Science 303 1782-1784

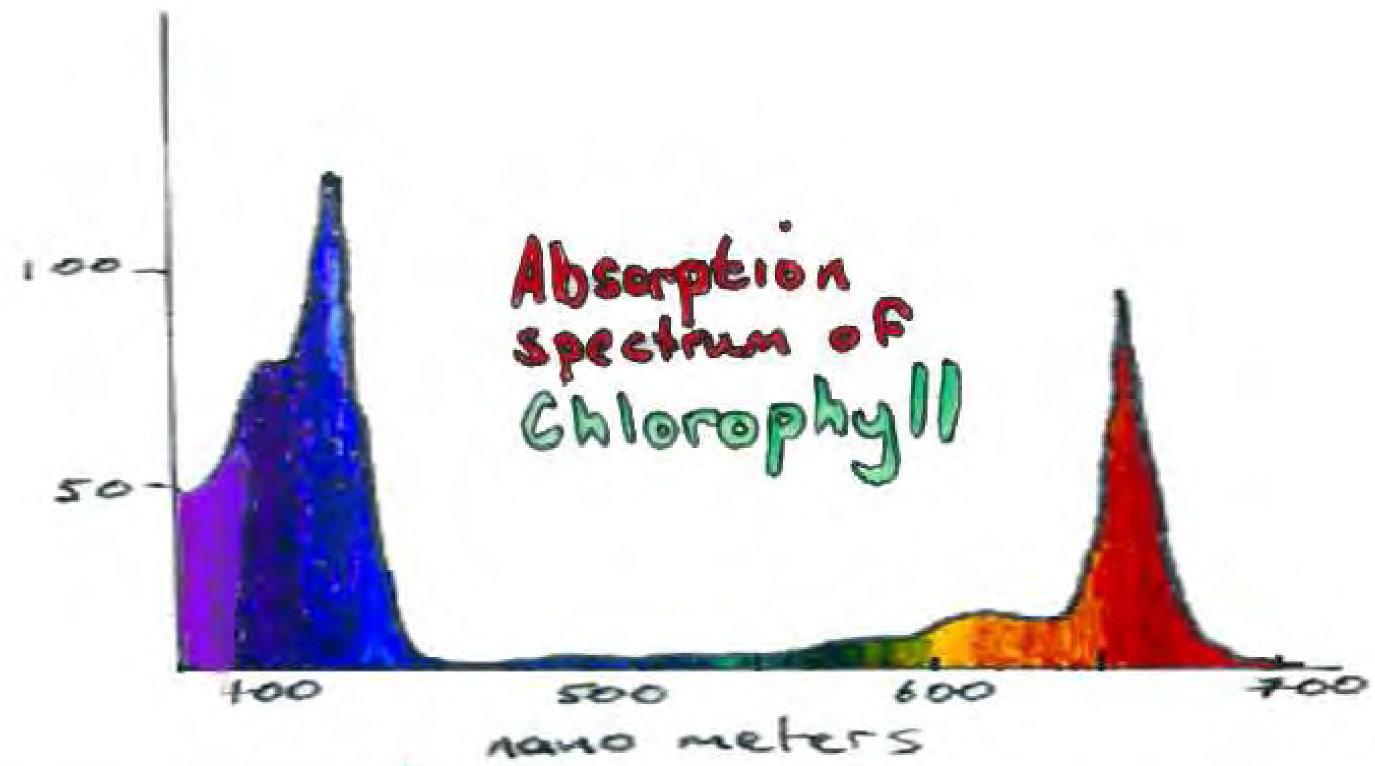

a leaf
a leaf section showing cells
a chloroplast section showing thylakoid membranes
a membrane section showing chlorophyll containing proteins
MEMBRANE PROTEINS
Antenna
Reaction Centre
MEMBRANE
Chlorophyll

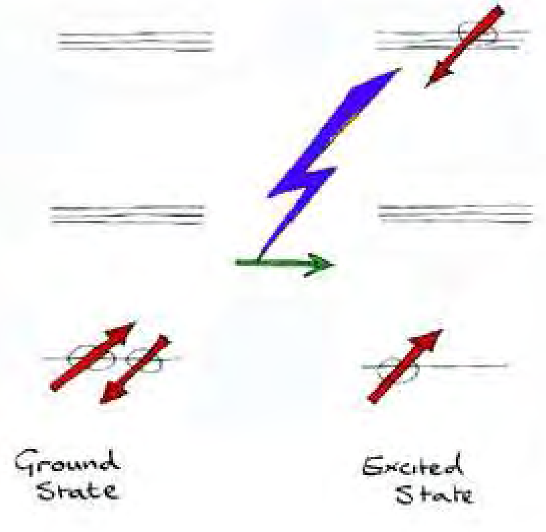


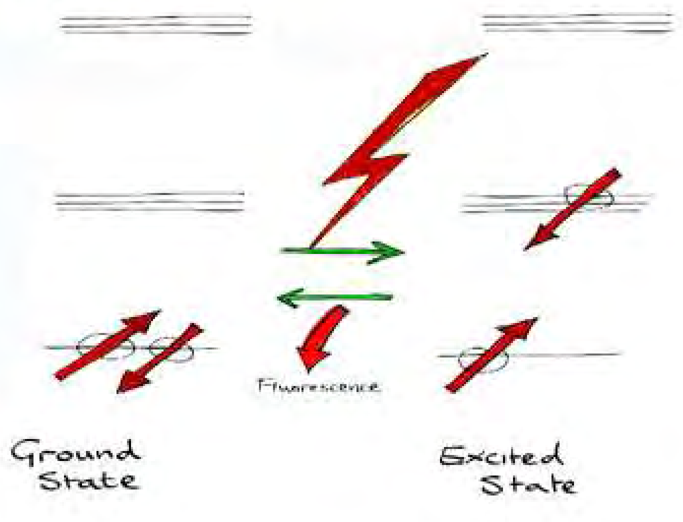
Excitation by light
A quantum of red light
lowest unoccupied molecular orbital
highest occupied molecular orbital
Fluorescence
Ground State
Excited State

Excitation by blue light



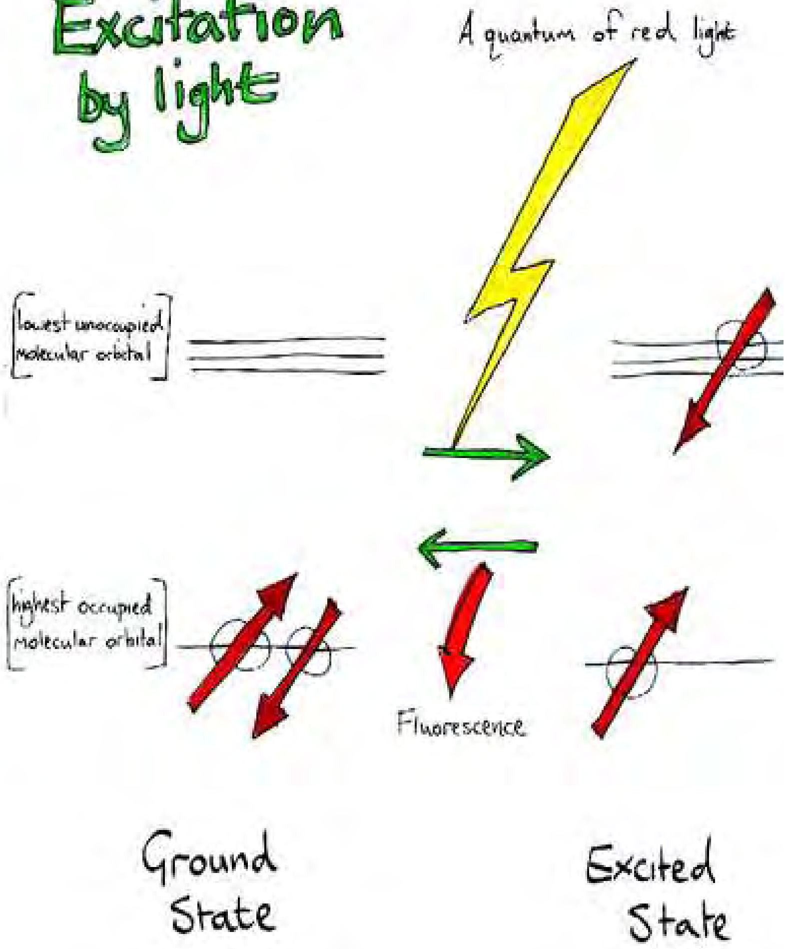

100
50
Absorption spectrum of Chlorophyll
400
500
600
700
nano meters


Ground State
Excited State


Fluorescence
Ground State
Excited State

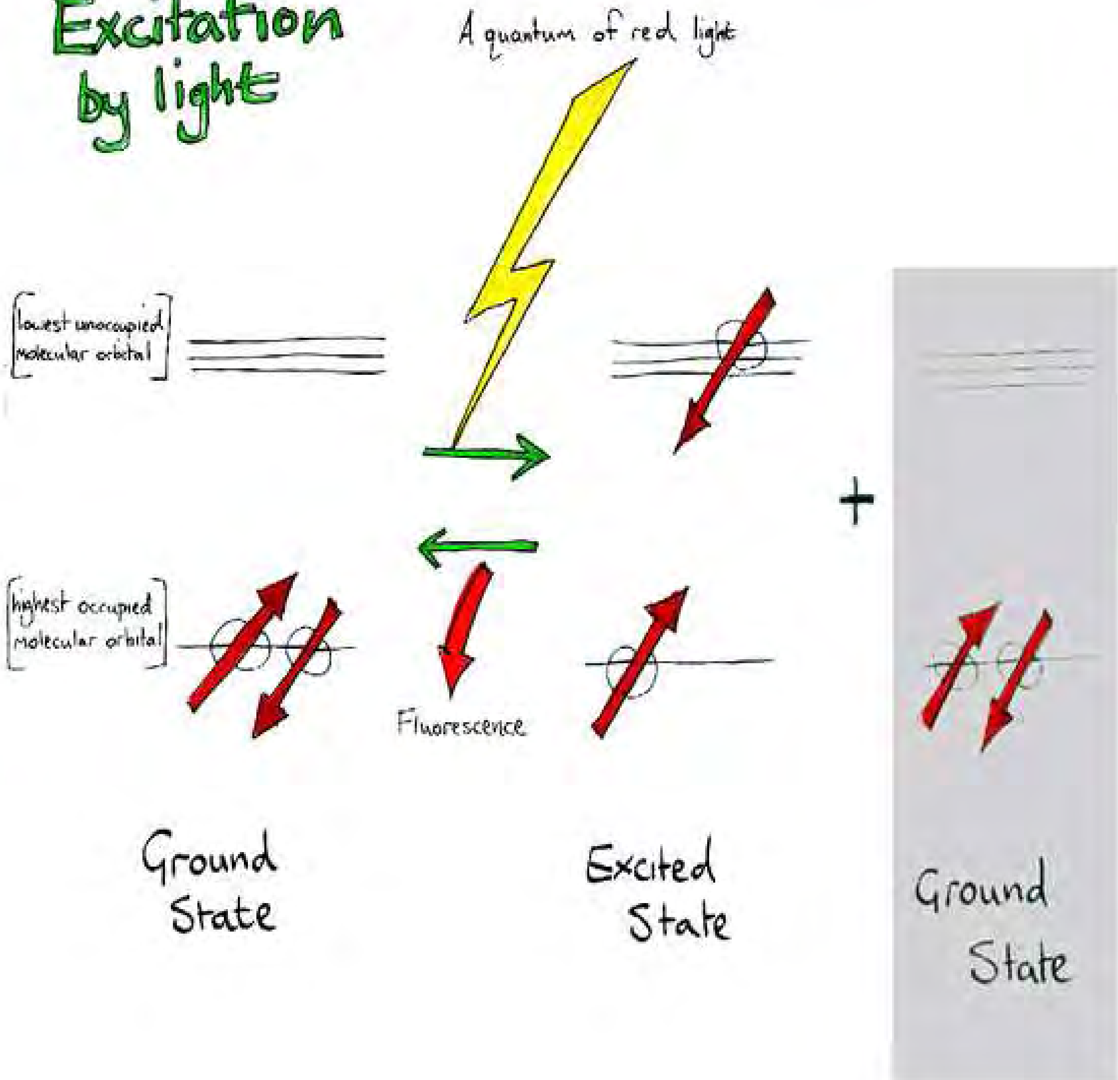
In light-collecting proteins

Excitation by light

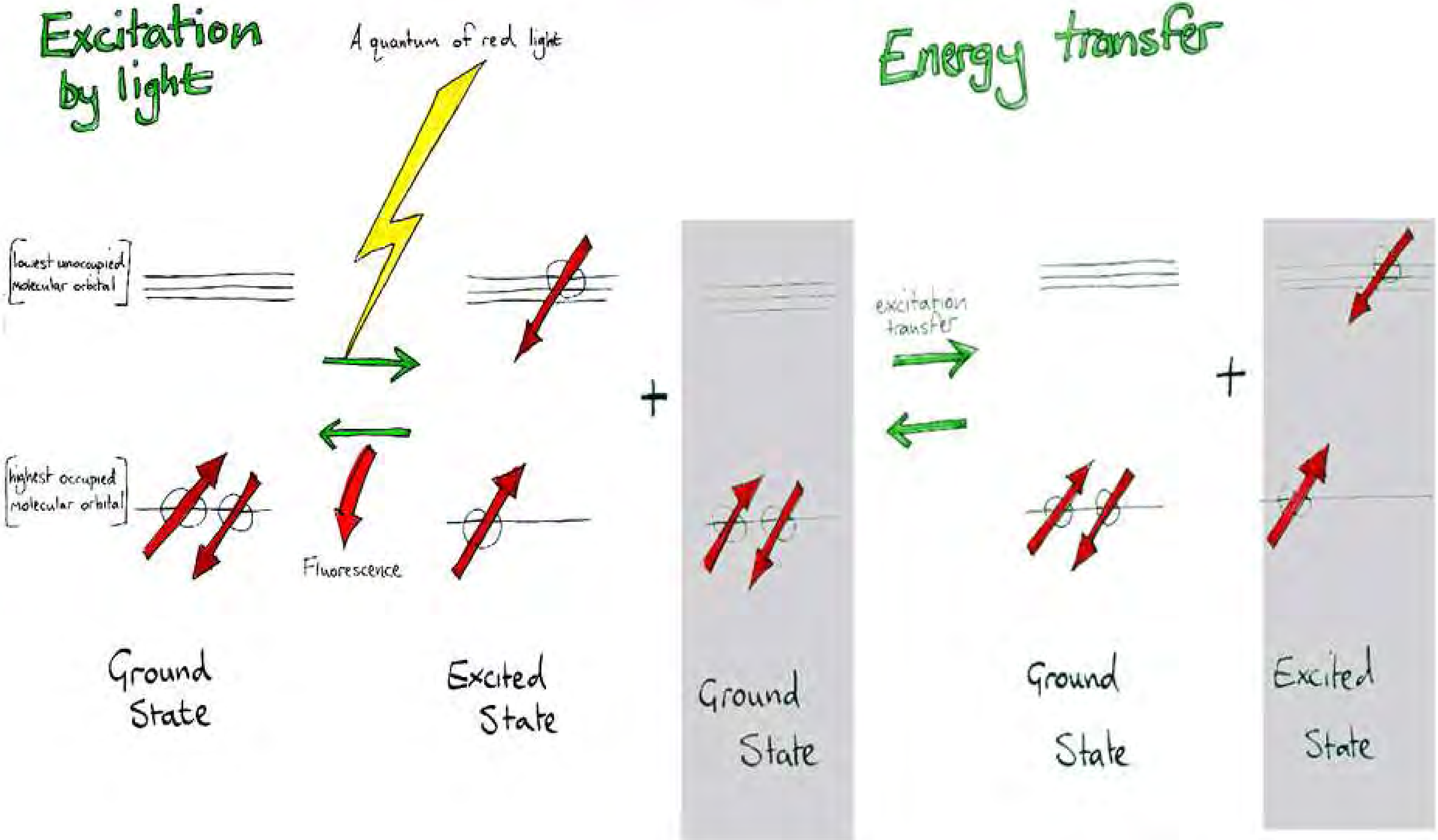


In light-collecting proteins

Excitation by light

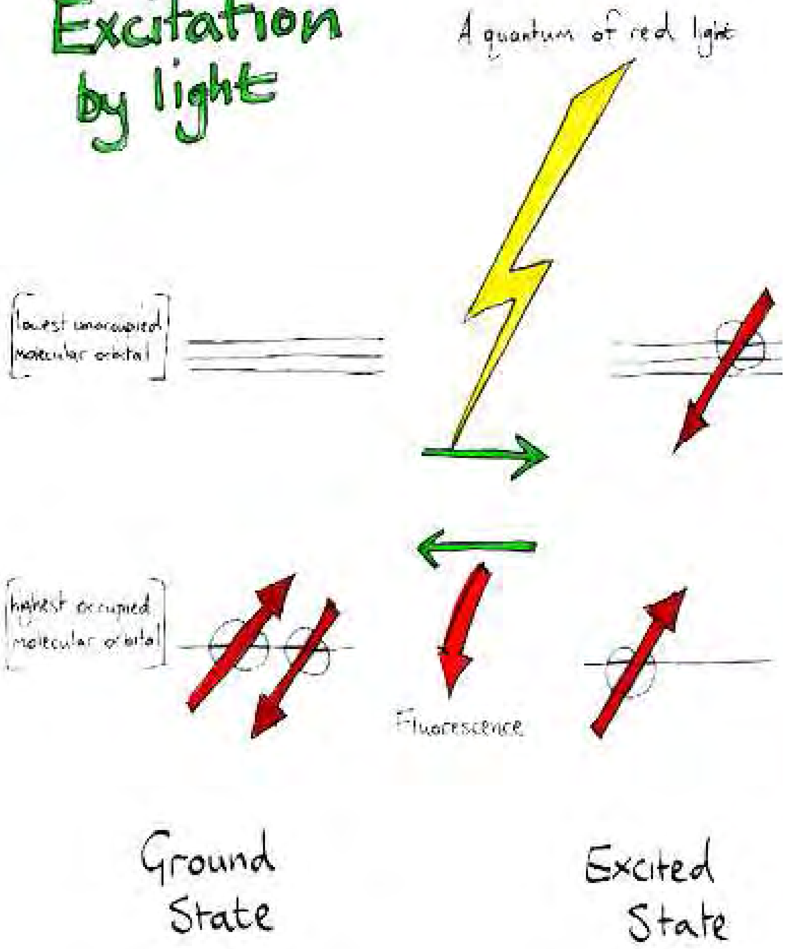


In light-collecting proteins



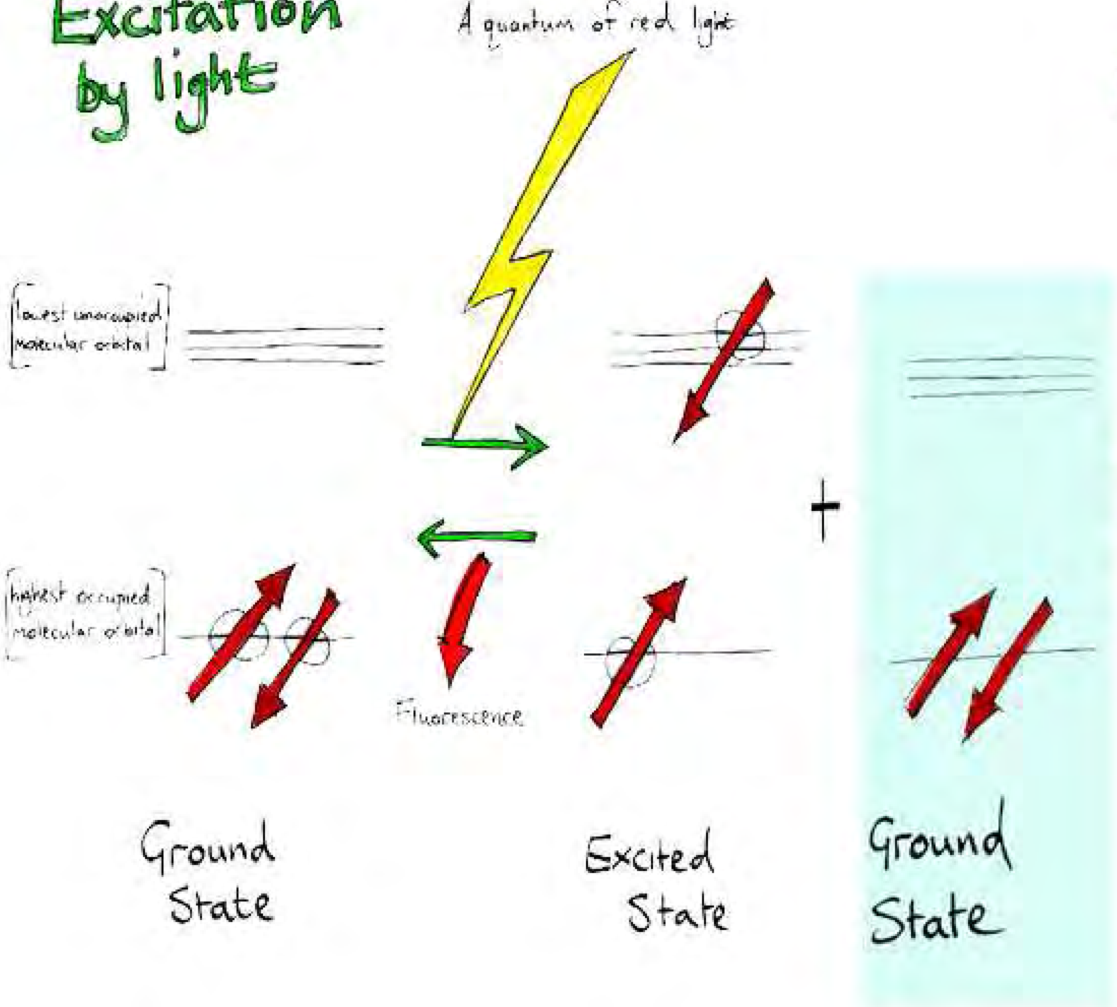
In reaction centre proteins

Excitation by light

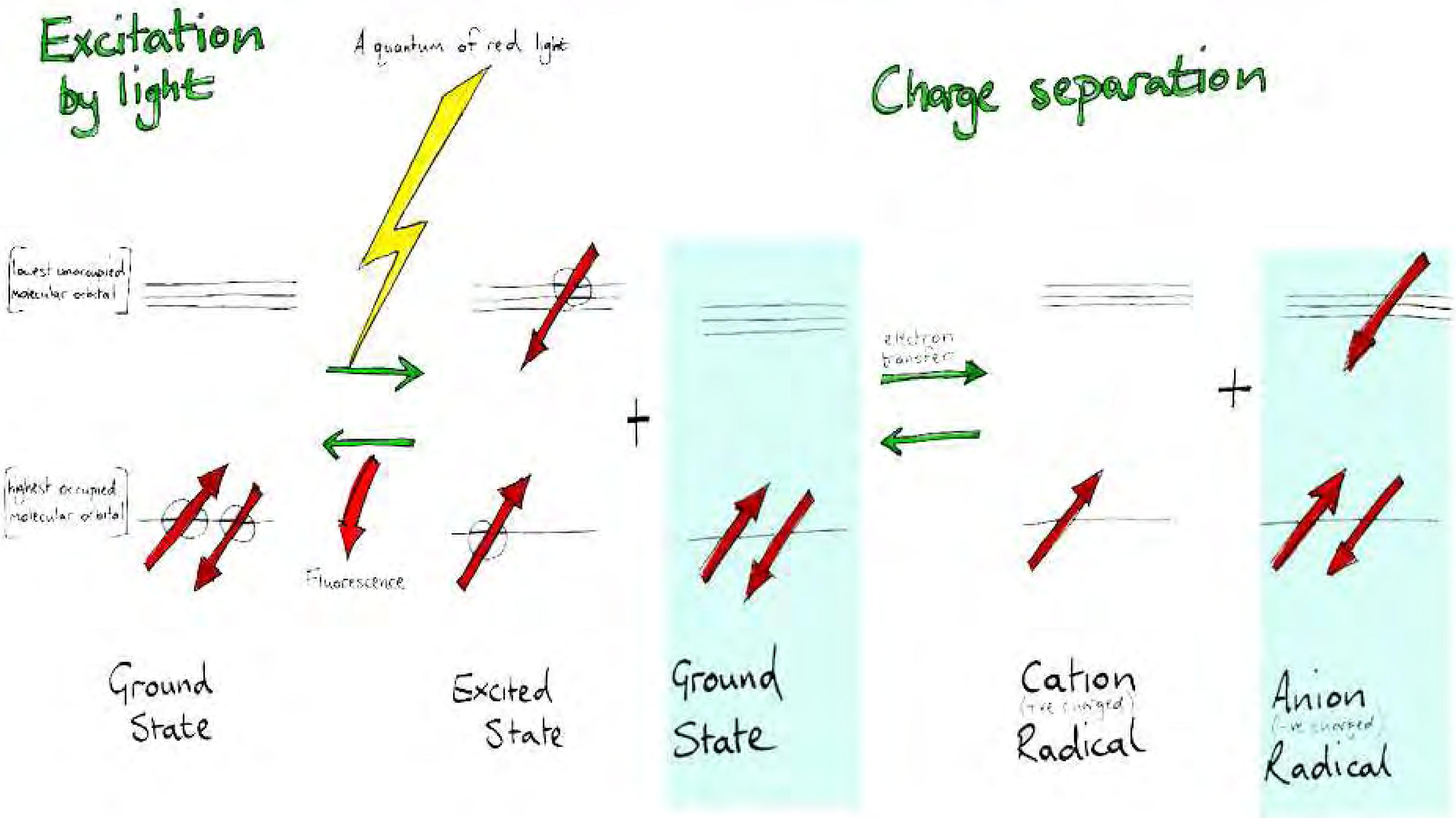


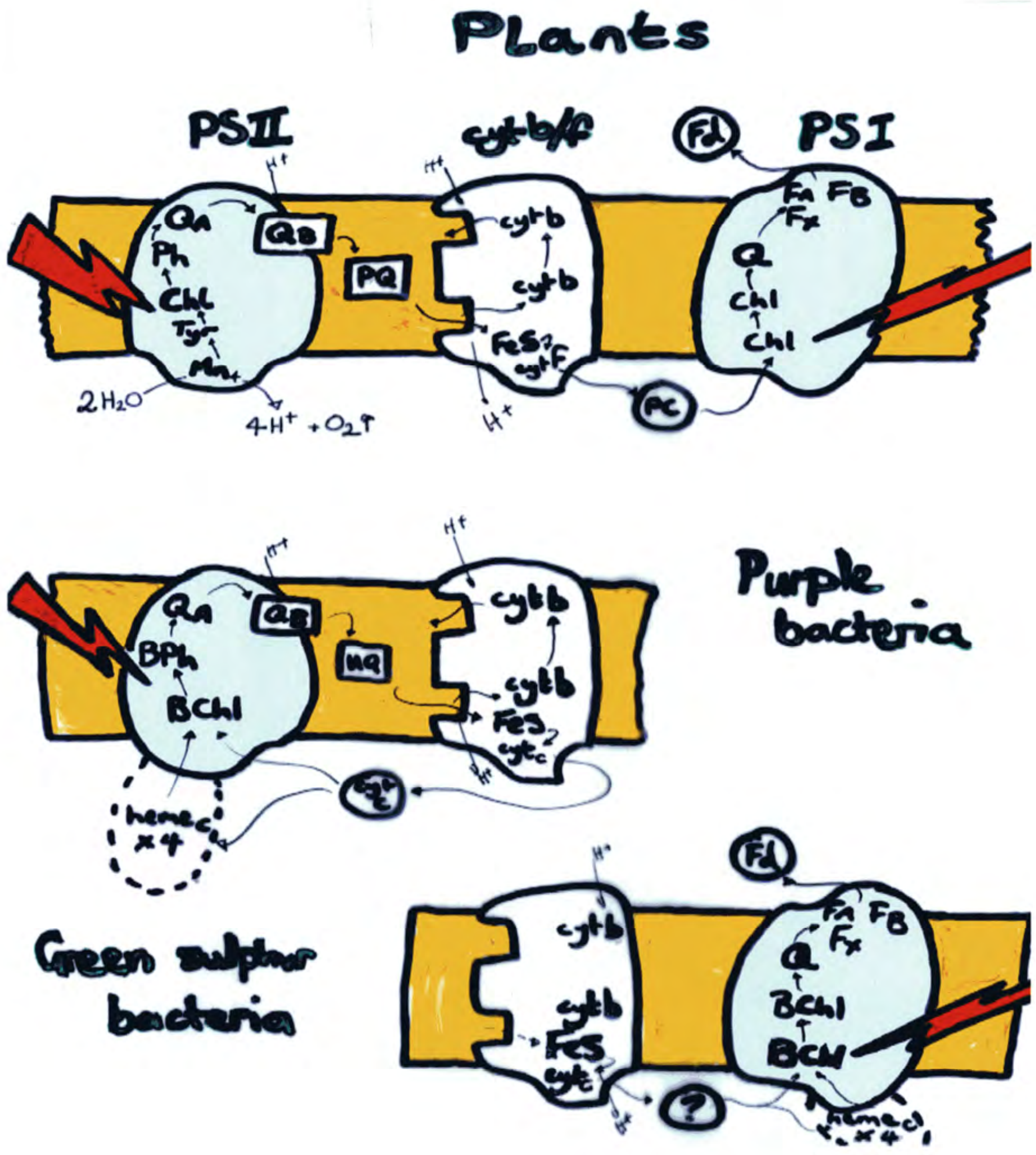
In reaction centre proteins

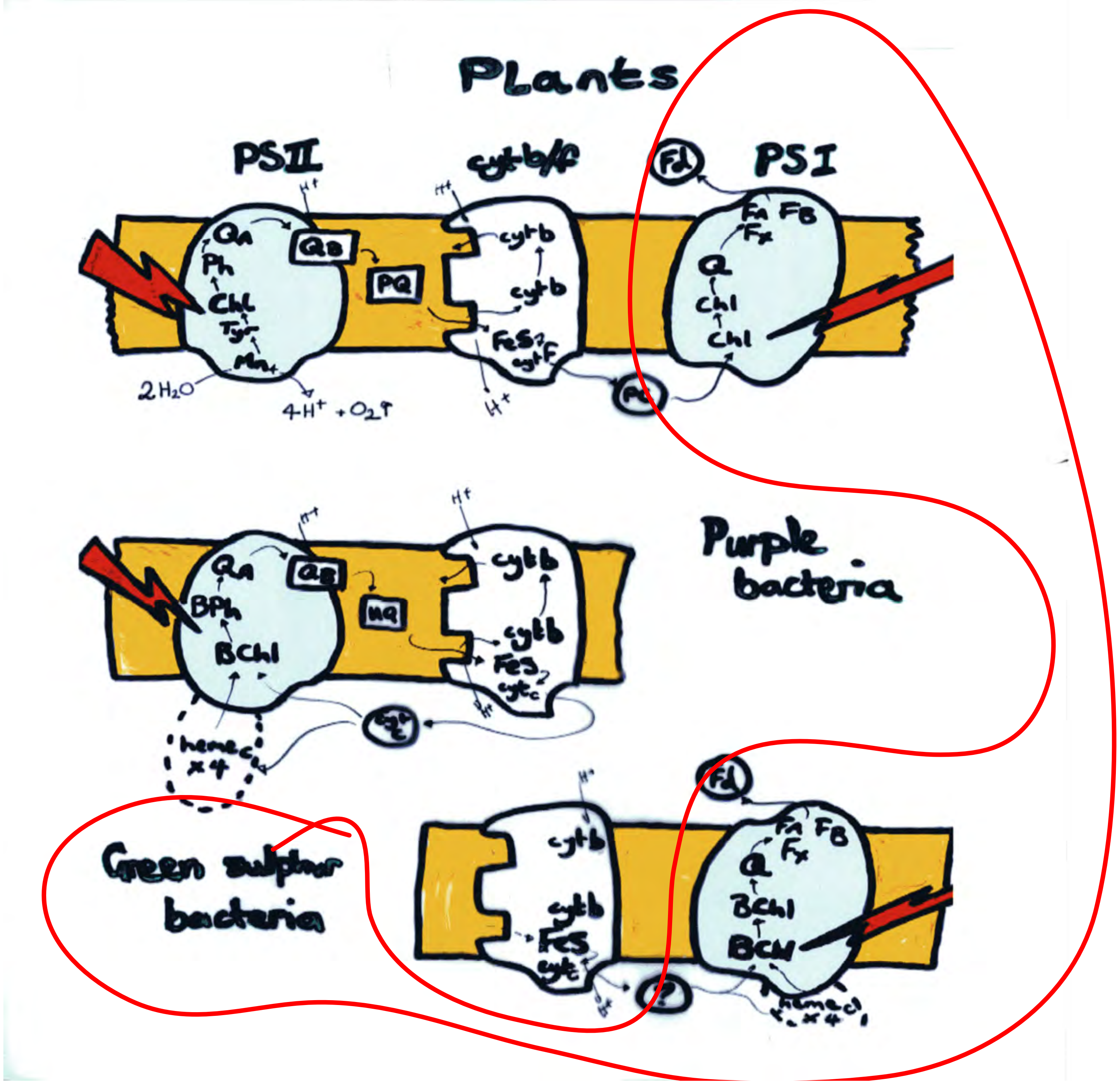
Excitation by light

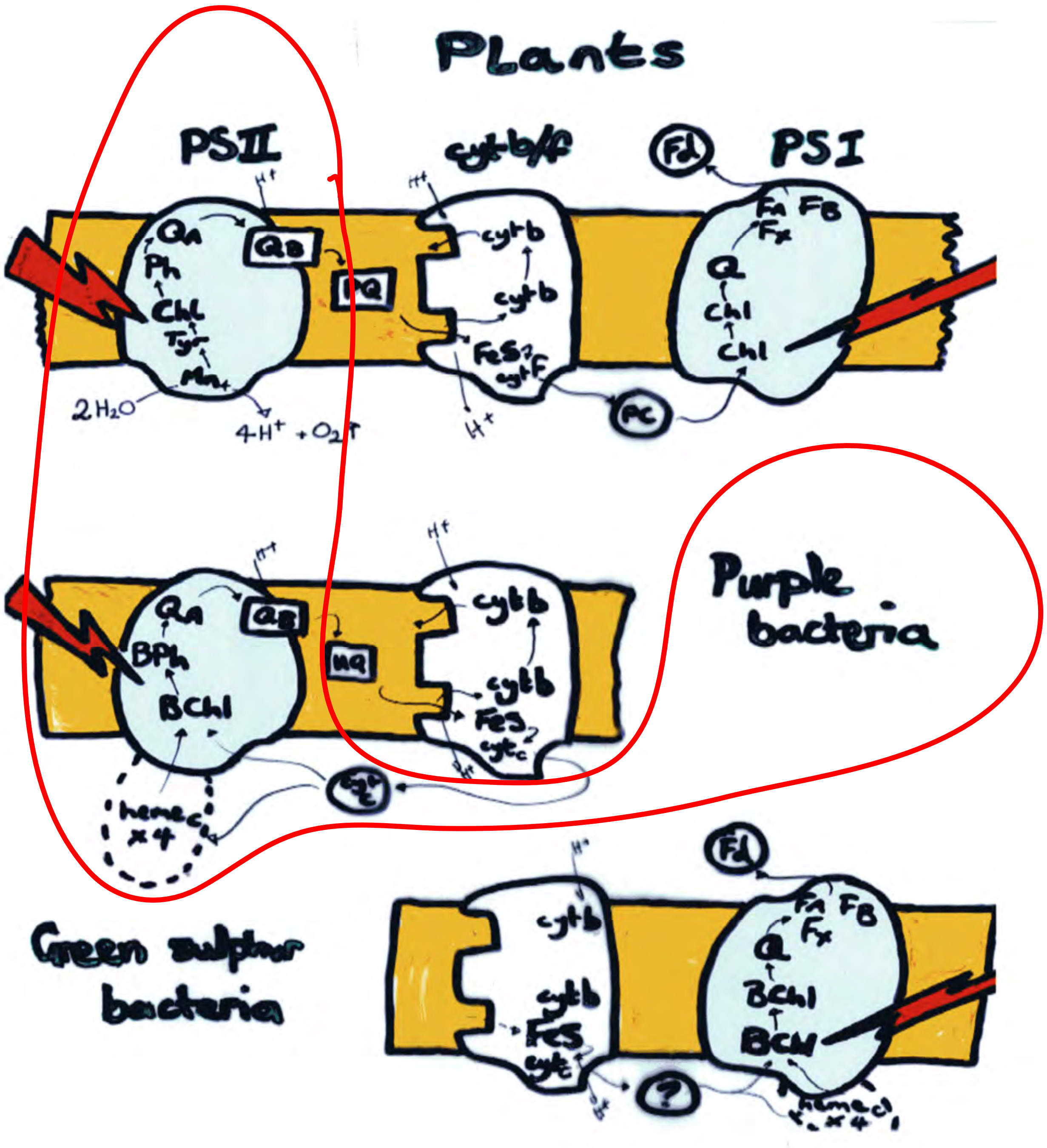


In reaction centre proteins



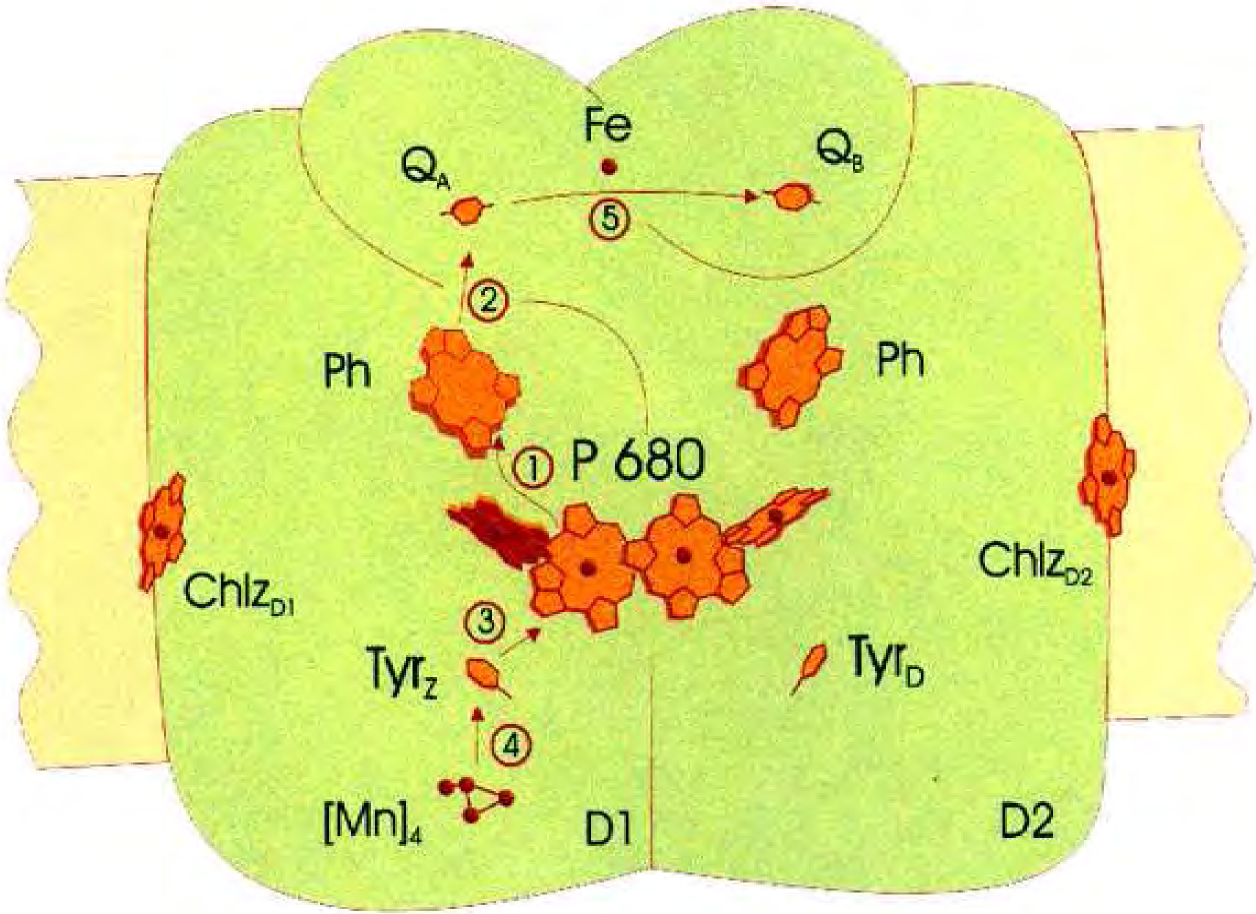

Plants
PSII
cyt b/f
Fd
PSI
H+
QA
QB
Ph
PQ
Chl
Tyr
Mn4
2H2O
4H+ + O2↑
cyt b
cyt b
FeS2
cyt F
PC
FA FB
Fx
Q
Chl
Chl
Purple bacteria
QA
QB
BPh
nQ
BChl
cyt b
cyt b
FeS2
cyt c
cyt c
heme c
x4
Green sulphur bacteria
Fd
cyt b
cyt b
FeS
cyt c
?
FA FB
Fx
Q
BChl
BChl
heme c
x4


Plants
PSII
cyt b/f
Fd
PSI
Qa
QB
Ph
Chl
Tyr
Mn4
PQ
cyt b
cyt b
FeS
cyt F
PC
FA FB
Fx
Q
Chl
Chl
2H2O
4H+ + O2
H+
Purple bacteria
Qa
QB
BPh
BChl
nq
cyt b
cyt b
FeS
cyt c2
cyt c2
heme c x4
Green sulphur bacteria
cyt b
cyt b
FeS
cyt c
?
Fd
FA FB
Fx
Q
BChl
BChl
heme c x4



Plants
PSII
cyt b/f
Fd
PSI
QA
QB
Ph
Chl
Tyr
Mn4
PQ
2H2O
4H+ + O2
H+
cyt b
cyt b
FeS?
cyt f
PC
FA FB
Fx
Q
Chl
Chl
Purple bacteria
QA
QB
BPh
BChl
cyt b
cyt b
FeS?
cyt c
cyt c
heme c x4
Green sulphur bacteria
Fd
cyt b
cyt b
FeS
cyt c
?
FA FB
Fx
Q
BChl
BChl
heme c x4

Photosystem II



the water oxidizing enzyme

Photosystem II

also known as: PSII, PS2, water oxidizing complex, oxygen evolving enzyme etc

Enzyme name:

Water/Plastoquinone photo oxidoreductase

Overall reaction catalysed:

$$2H_2O + 2PQ \longrightarrow 2PQH_2 + O_2\uparrow$$

(PQ: plastoquinone; PQH_2: plastoquinol)

half reactions

1 water oxidation

$$2H_2O \longrightarrow 4H^+ + 4e^- + O_2 \quad (E_{m_7}\ +820\,mV)$$

2 quinone reduction

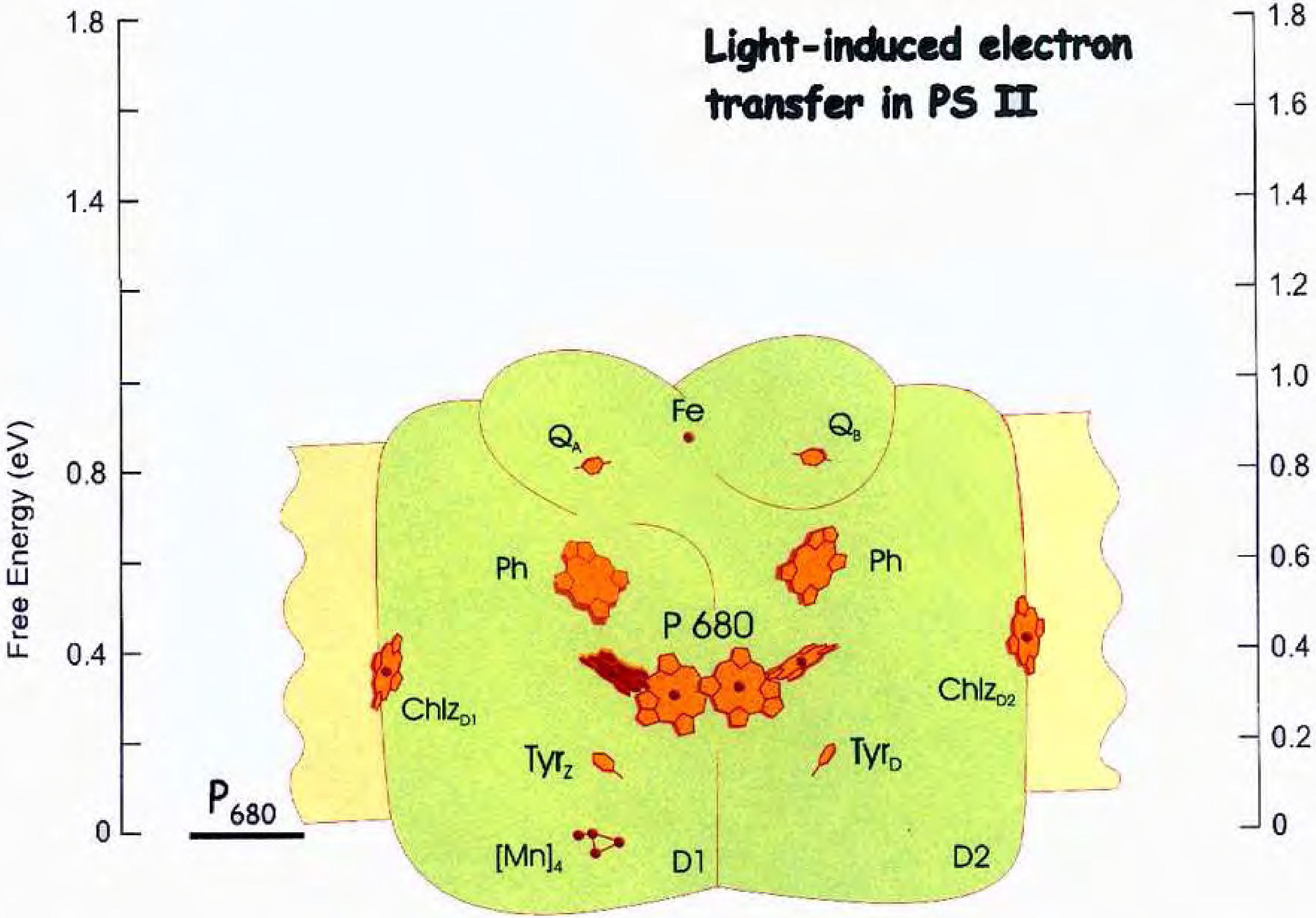
$$PQ + 2e^- + 2H^+ \longrightarrow PQH_2 \quad (E_{m_7}\ +120\,mV)$$

$\Delta E = -700\,mV$

($\Delta G \approx -70\,kJ/mole$ electrons)

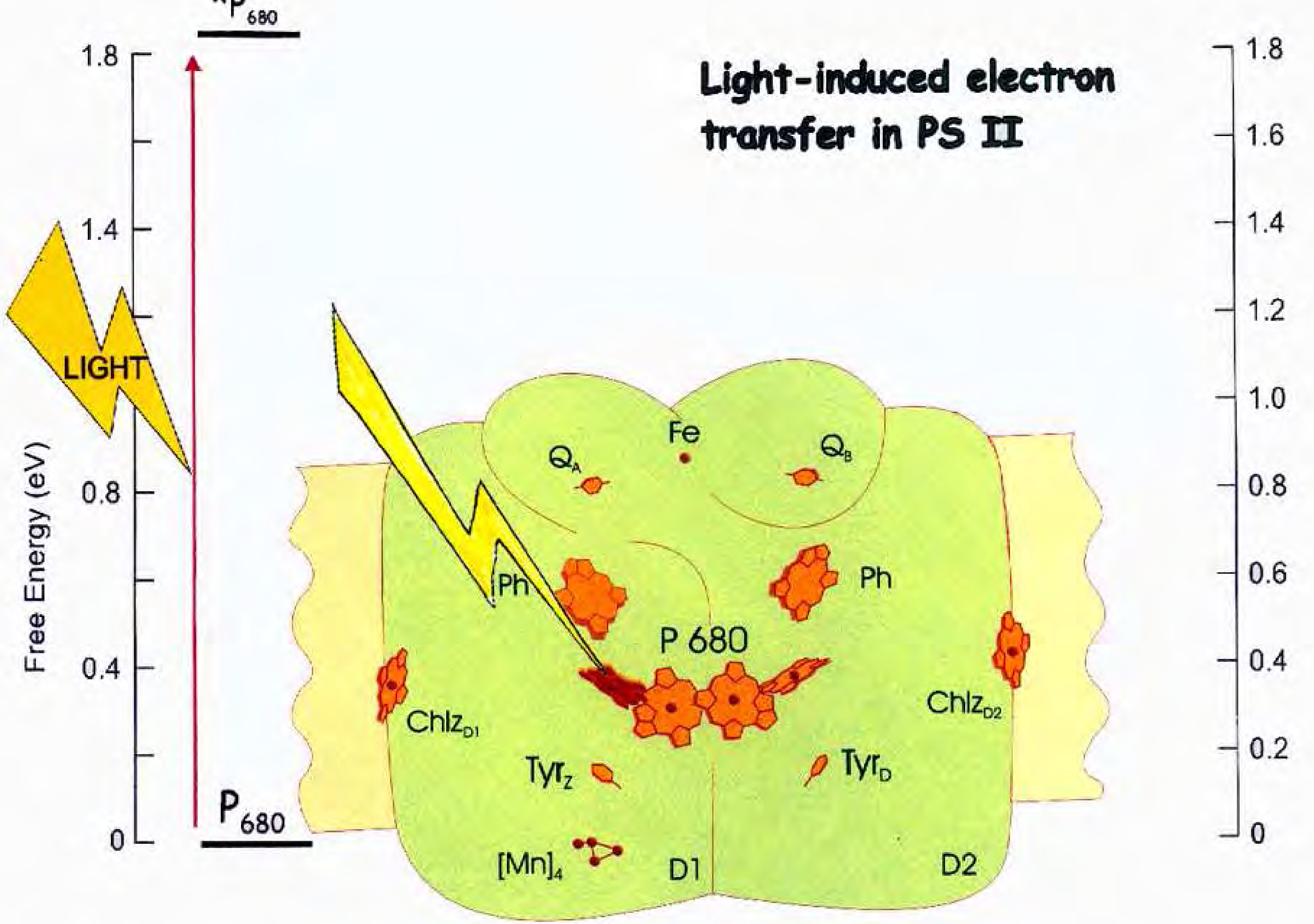
reaction requires big energy input: **light**

nb. 680nm = 1.82V

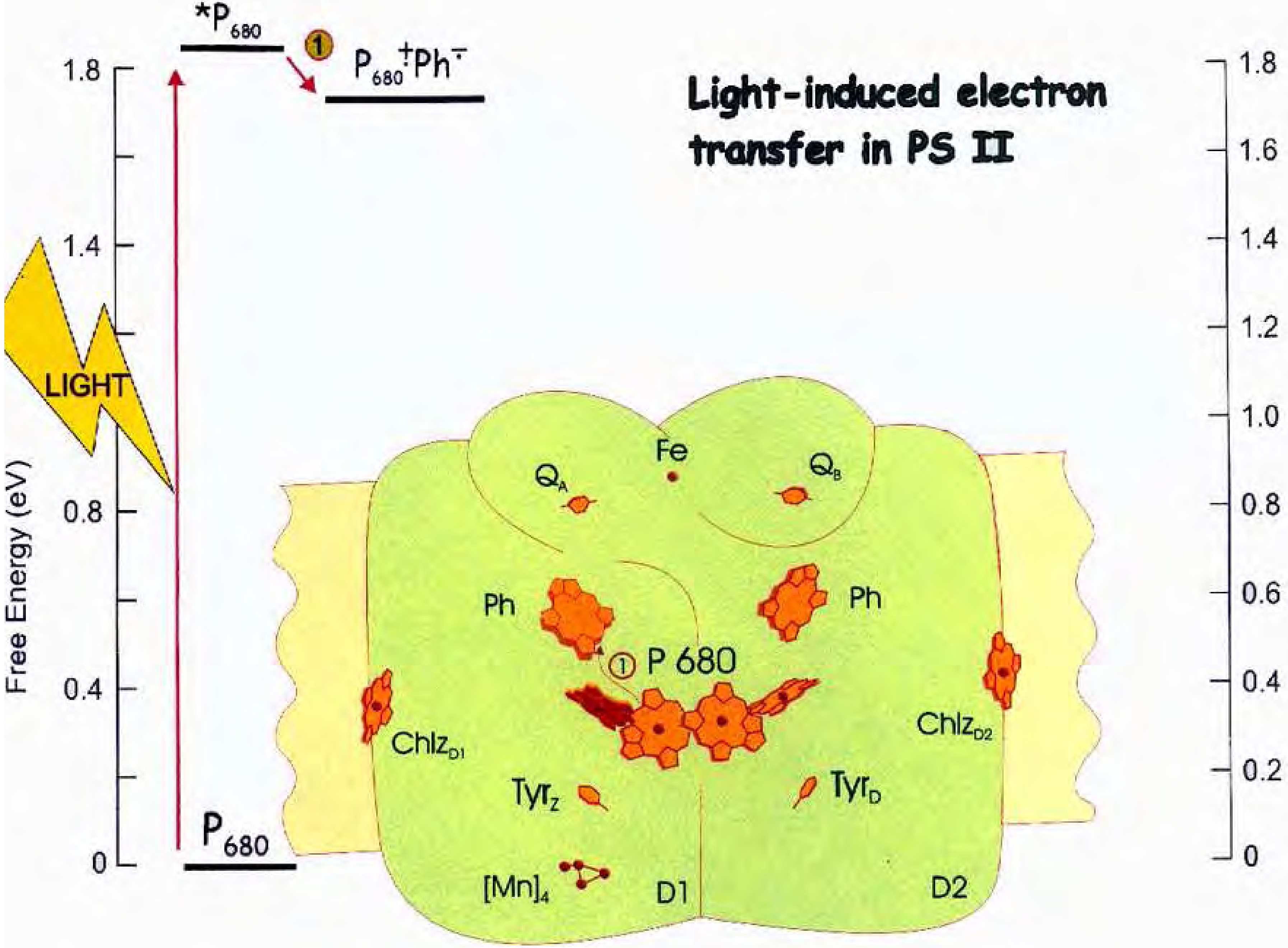


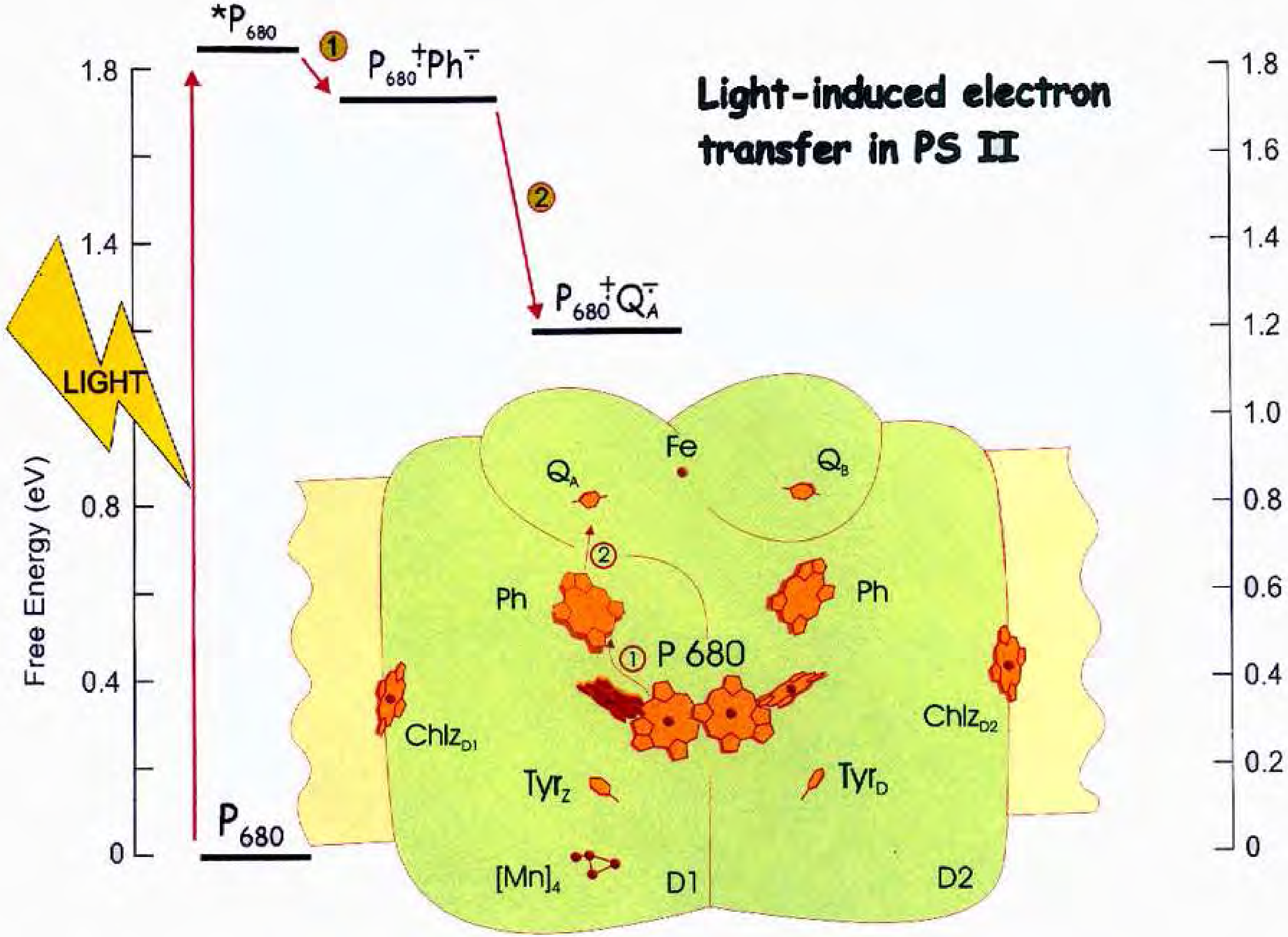
Light-induced electron transfer in PS II
Free Energy (eV)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
Fe
Q_A
Q_B
Ph
Ph
P 680
$Chlz_{D1}$
$Chlz_{D2}$
Tyr_Z
Tyr_D
$[Mn]_4$
D1
D2
P_{680}

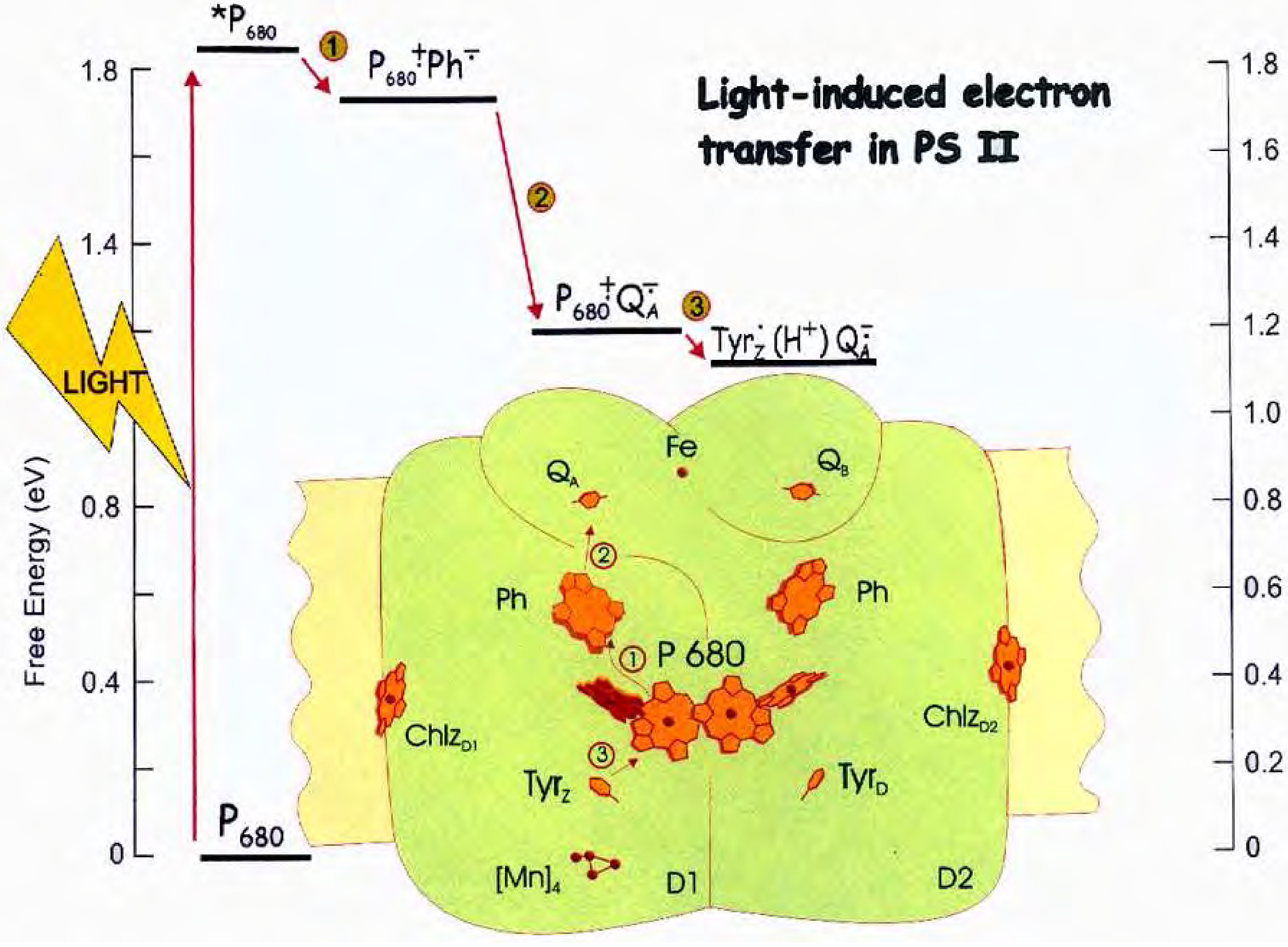
Light-induced electron transfer in PS II



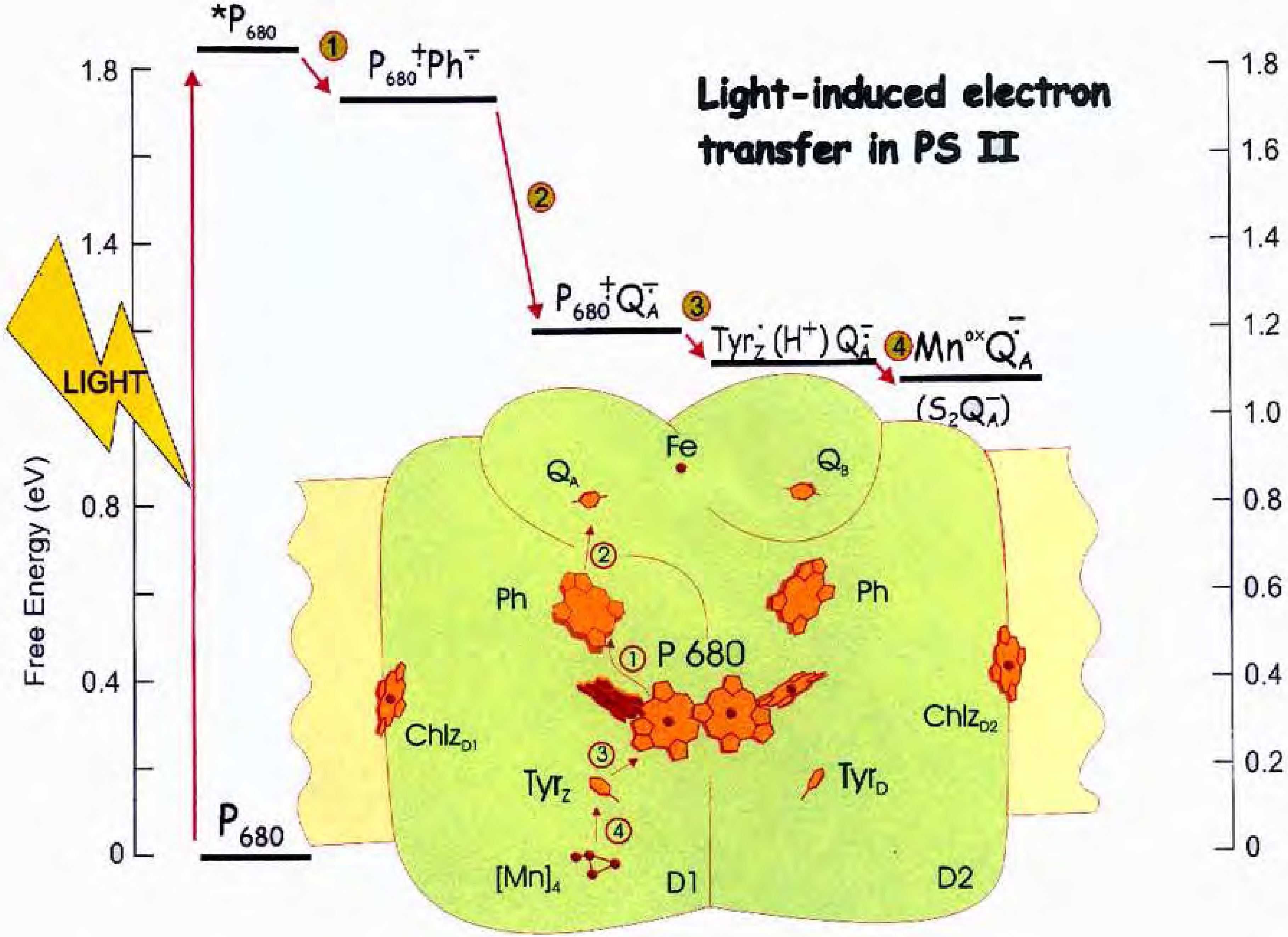
Light-induced electron transfer in PS II



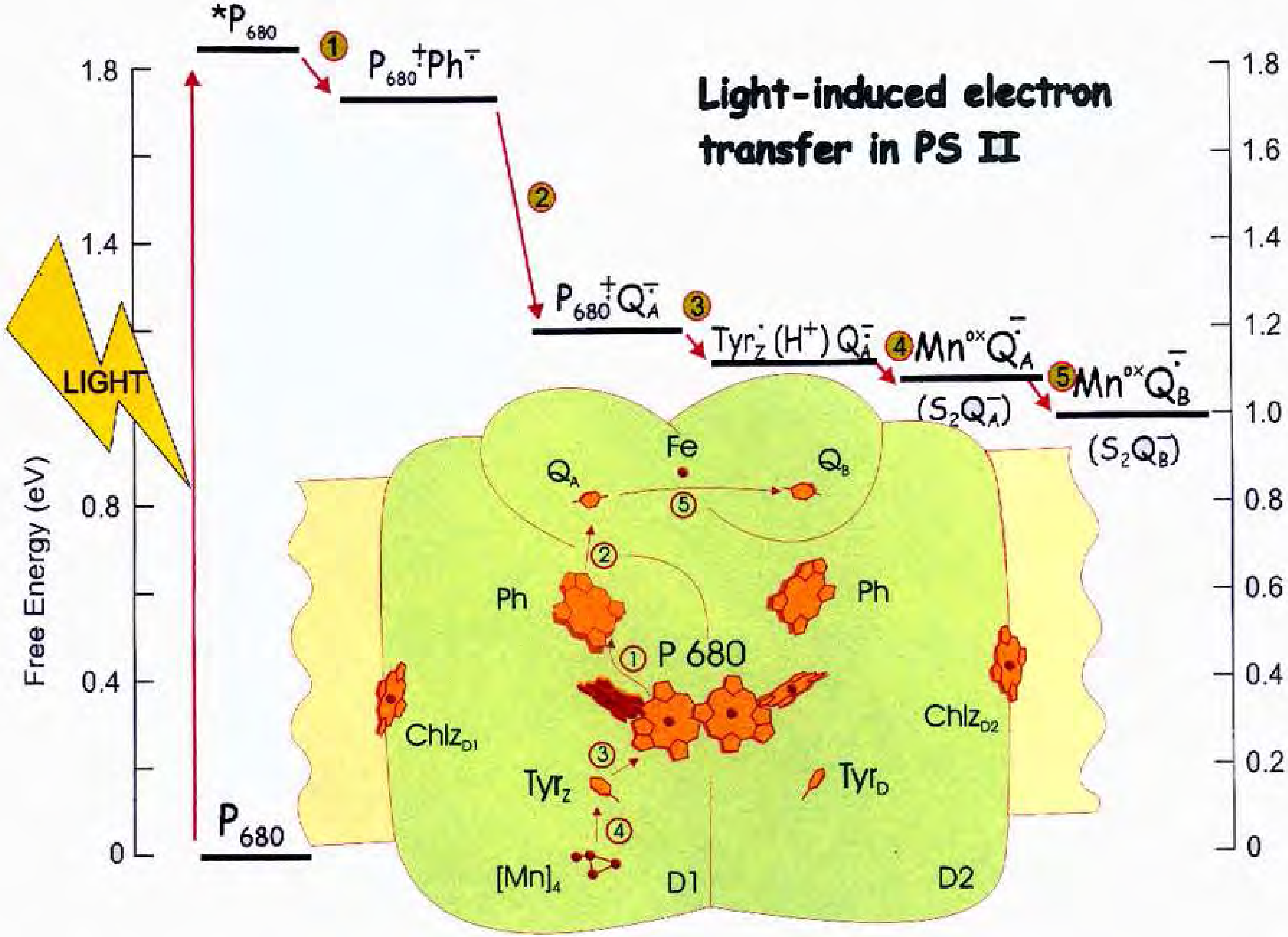

Light-induced electron transfer in PS II
*P680
P680+Ph−
P680+QA−
P680
1
2
LIGHT
Free Energy (eV)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
Fe
QA
QB
Ph
Ph
P 680
ChlzD1
ChlzD2
TyrZ
TyrD
[Mn]4
D1
D2



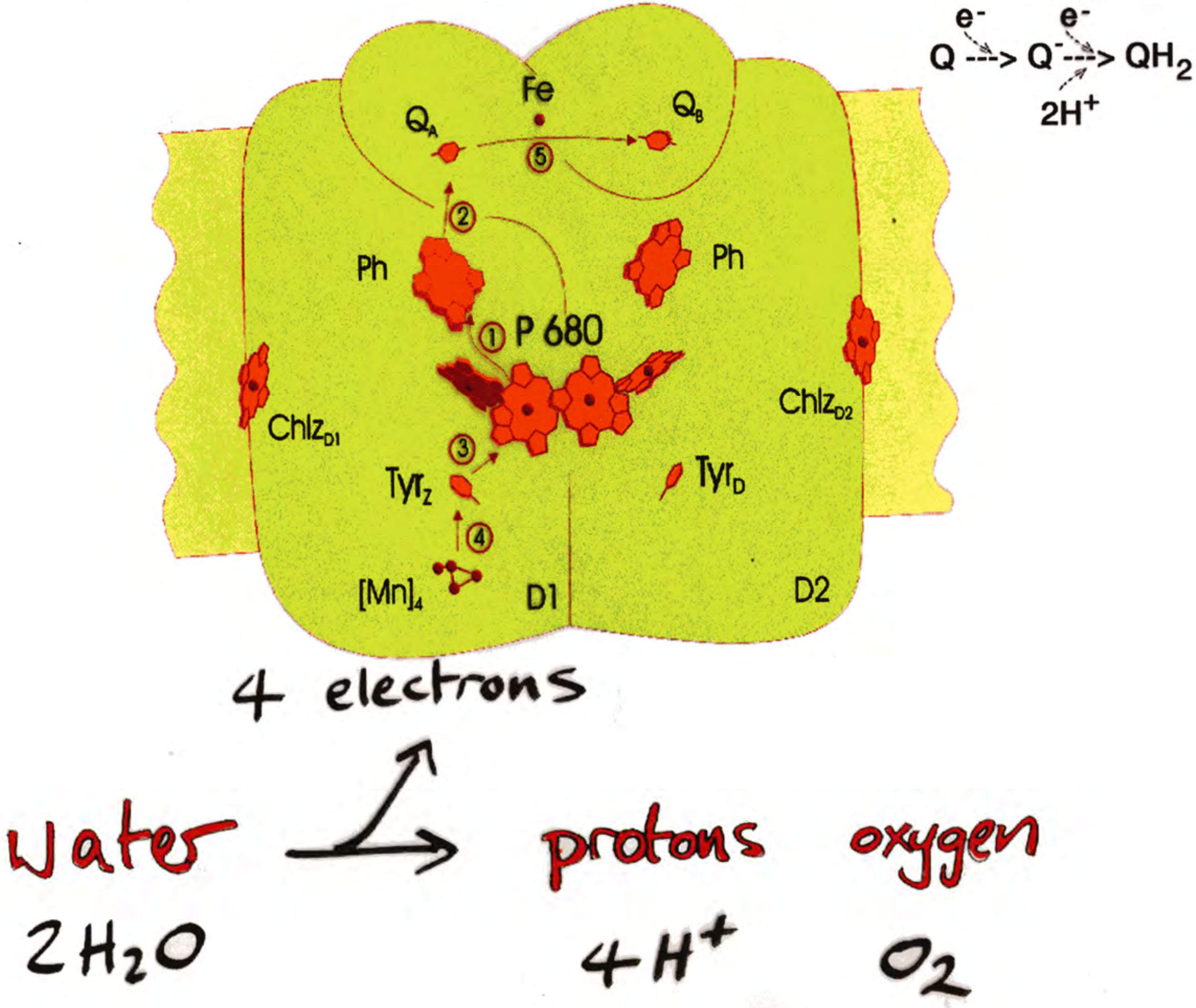
Light-induced electron transfer in PS II
Free Energy (eV)
1.8
1.4
0.8
0.4
0
1.6
1.2
1.0
0.6
0.2
LIGHT
*P680
1
P680+Ph−
2
P680+QA−
3
Tyrz (H+) QA−
P680
Fe
QA
QB
Ph
Ph
P 680
ChlzD1
ChlzD2
Tyrz
TyrD
[Mn]4
D1
D2



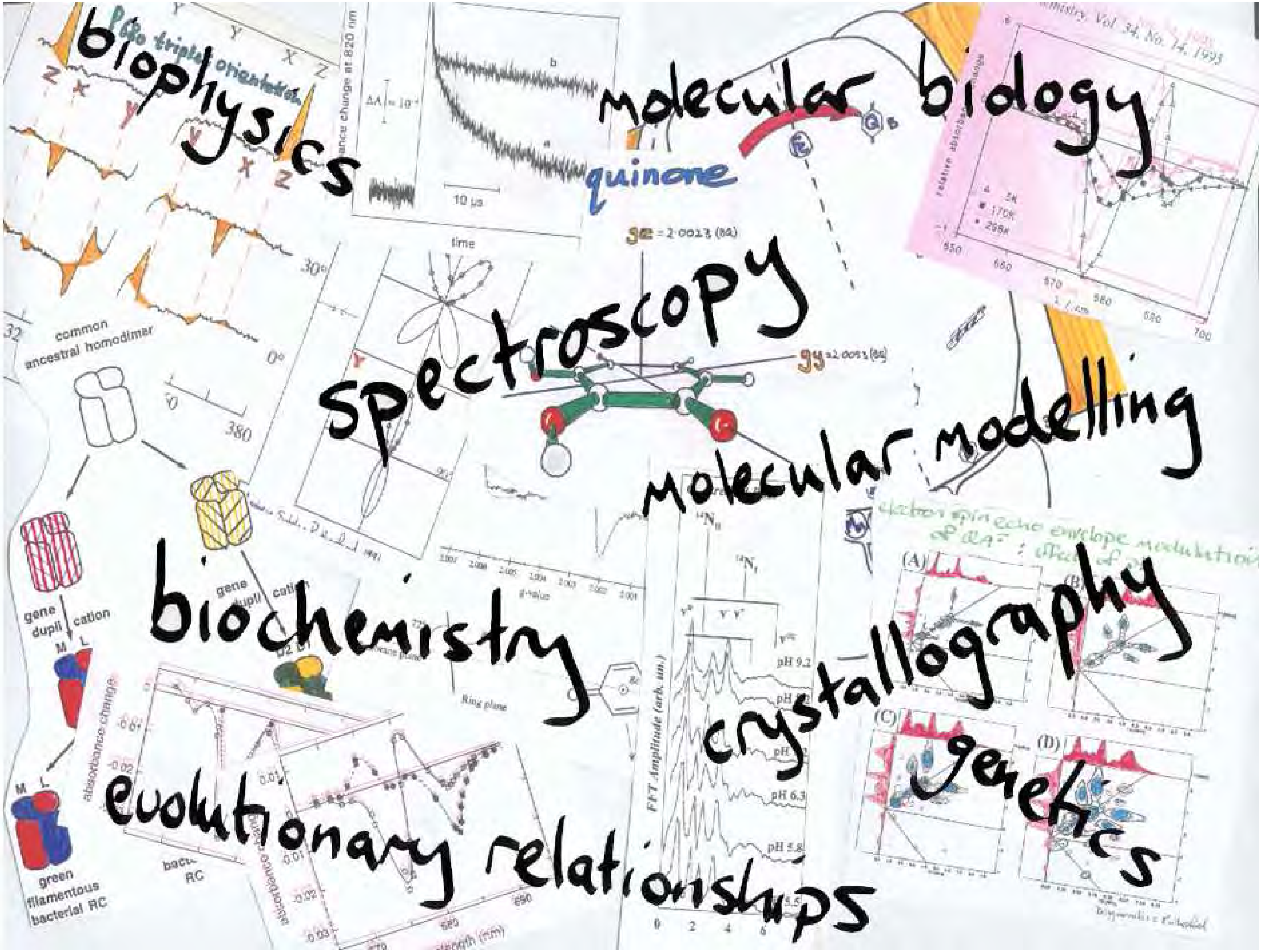
Light-induced electron transfer in PS II
*P680
1
P680+Ph−
2
P680+QA−
3
Tyrz (H+) QA−
4
Mnox QA−
(S2QA−)
P680
LIGHT
Free Energy (eV)
1.8
1.4
1.2
0.8
0.4
0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
Fe
QA
QB
Ph
Ph
P 680
ChlzD1
ChlzD2
TyrZ
TyrD
[Mn]4
D1
D2



Light-induced electron transfer in PS II
*P680
P680+Ph−
P680+QA−
Tyrz (H+) QA−
Mn^ox QA−
(S2QA−)
Mn^ox QB−
(S2QB−)
LIGHT
P680
Free Energy (eV)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
Fe
QA
QB
Ph
Ph
P 680
ChlzD1
ChlzD2
TyrZ
TyrD
[Mn]4
D1
D2


e-
Q ---> Q- ---> QH2
2H+
Fe
QA
QB
5
2
Ph
Ph
1
P 680
ChlzD1
ChlzD2
3
TyrZ
TyrD
4
[Mn]4
D1
D2
4 electrons
water
protons
oxygen
2H2O
4H+
O2

- - - - but how do we know ?


biophysics
molecular biology
quinone
spectroscopy
molecular modelling
biochemistry
crystallography
genetics
evolutionary relationships
common ancestral homodimer
gene duplication
green filamentous bacterial RC
10 µs
time
pH 9.2
pH 6.3
pH 5.8

PS II is structurally similar to the purple bacterial reaction centre.

1. Spectroscopy — EPR; — Absorption
2. Amino acid sequence comparisons — herbicide resistance
3. Biochemistry — isolation of proteins
4. Mutagenesis — Tyrosines
5. Crystallography — helices; — chromophores; — protein

PS II is structurally similar to the purple bacterial reaction centre.

1 Spectroscopy — EPR — Absorption

2 Amino acid sequence comparisons — herbicide resistance

3 Biochemistry — isolation of proteins

4 Mutagenesis — Tyrosines

5 Crystallography — helices — chromophores — protein

Evolutionary relationships

Phase 1

discovering & identifying the cofactors

(comparative spectroscopy)

PSII is like a purple RC

the first signs

primary quinone

Witt, van Gorkom
etc
(Clayton, Lauch, Feher, Dutton)

secondary quinone

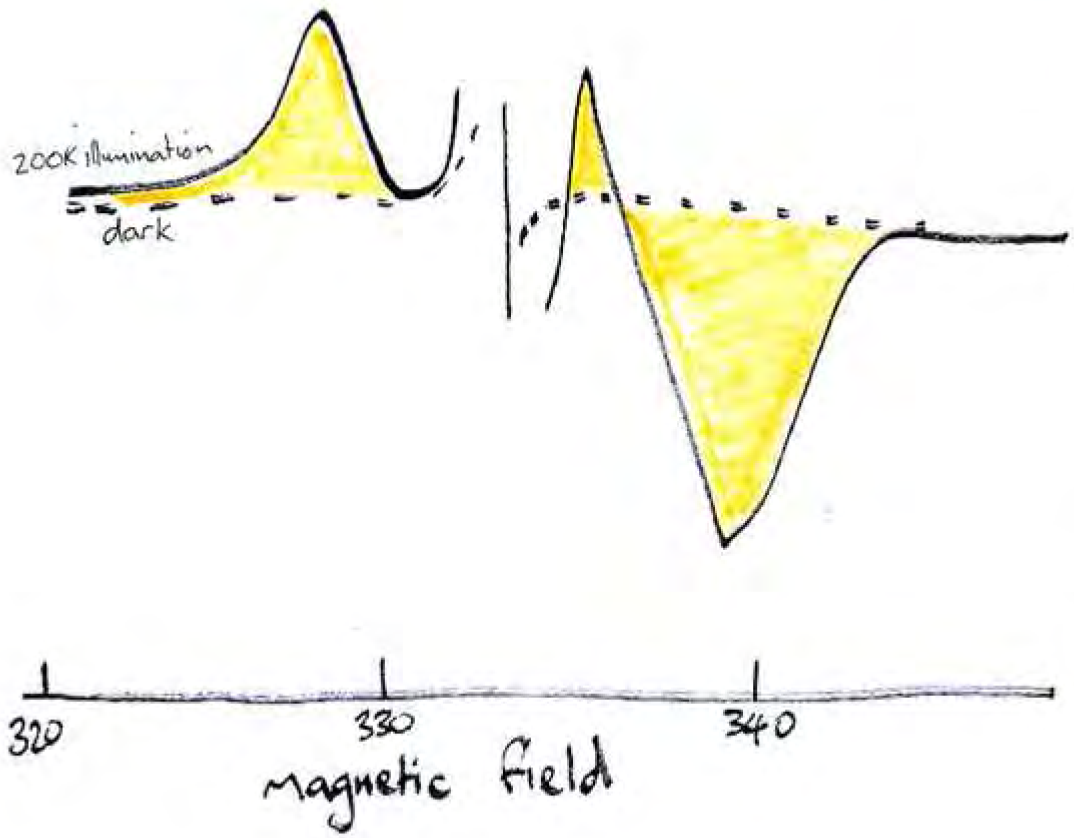
Bouges Bocquet 73
Velthuys 74
(Wraight 75, Vermeglio Clayton 75)

pheophytin

van Gorkom 74-75
Klimov ~76
(Tiede Dutton 75
etc)

Pheo$^-$ split signal in PSII

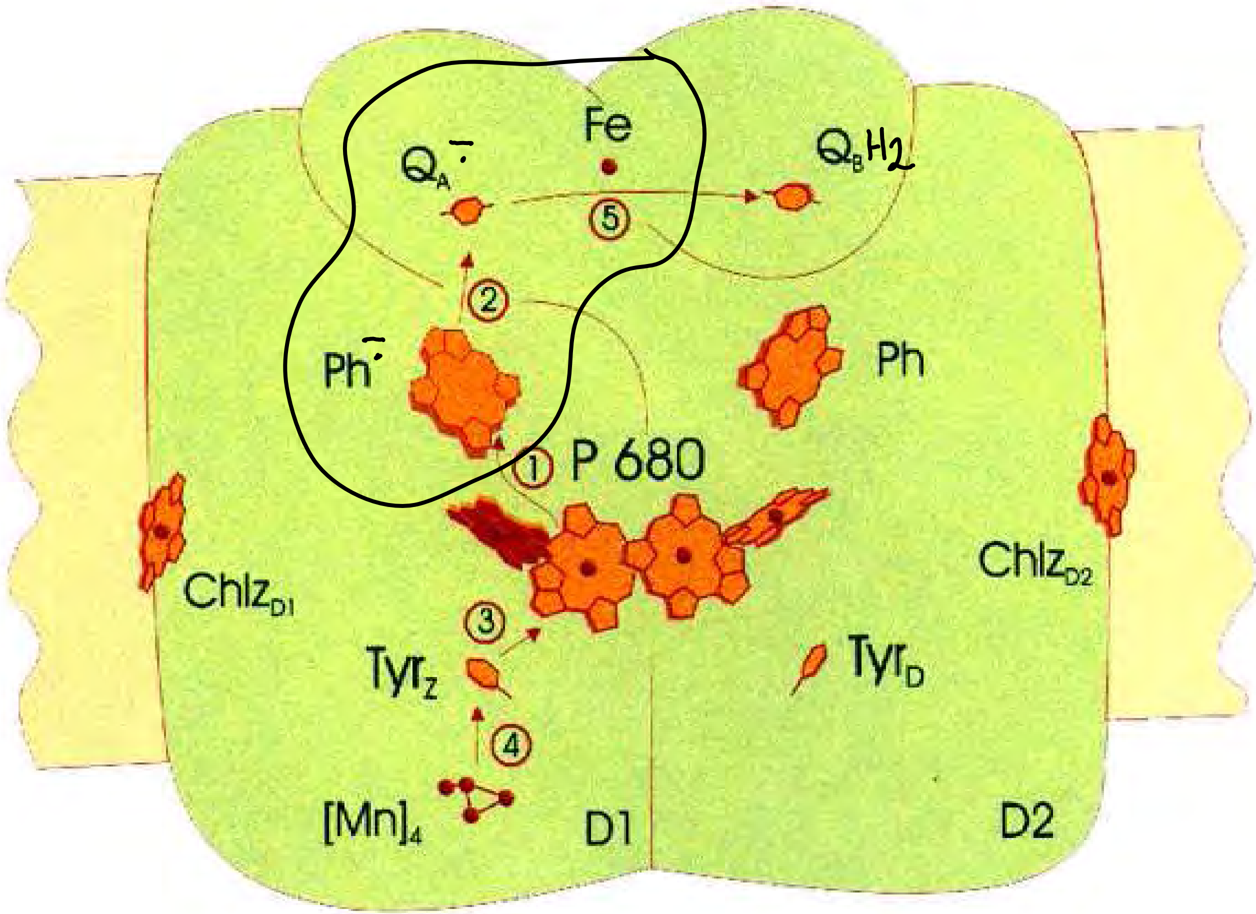
$Ph^{\dot{-}}\ Q_A^{\dot{-}}\ Fe^{2+}$

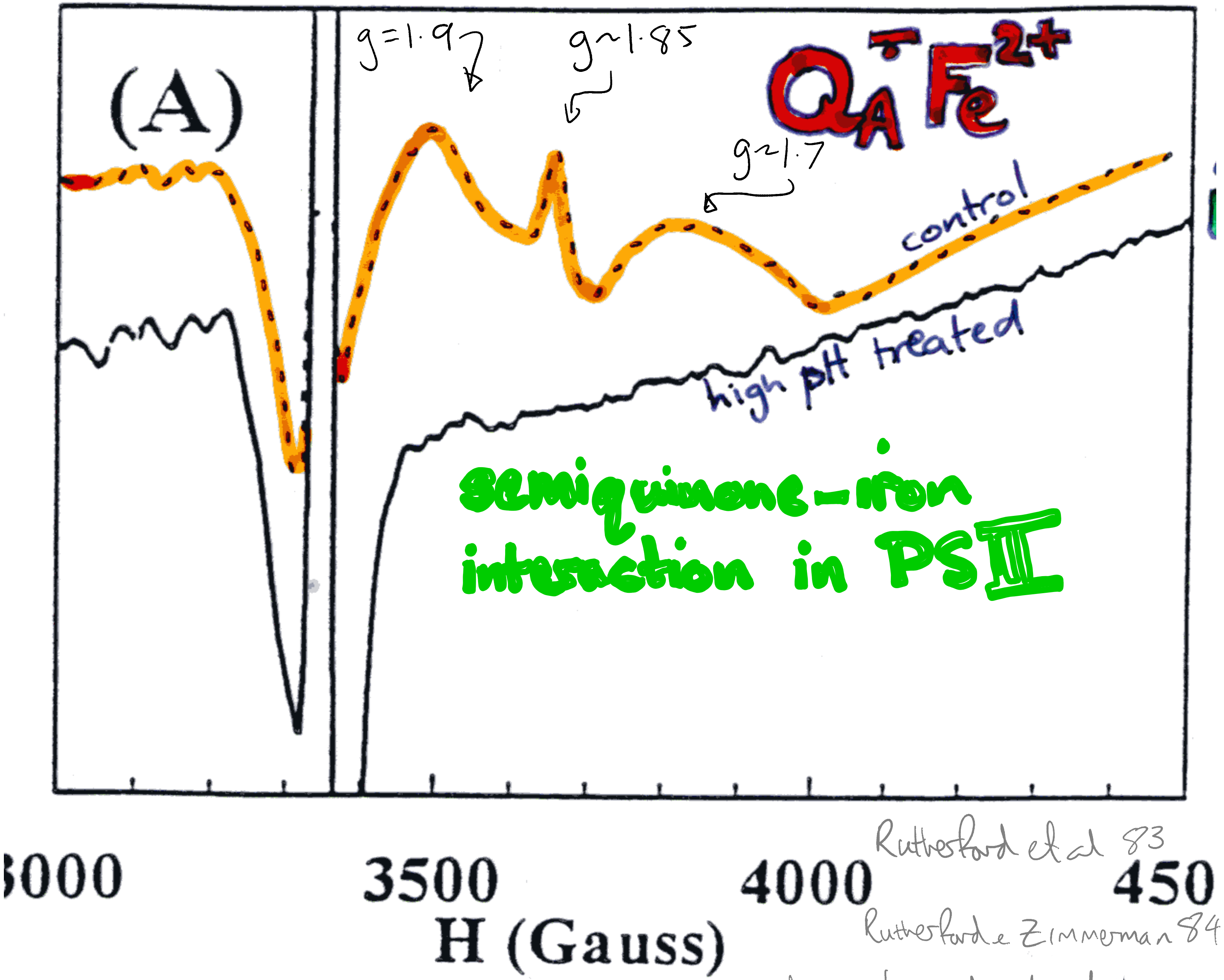


Klimov et al 80

Rutherford et al 80, 83

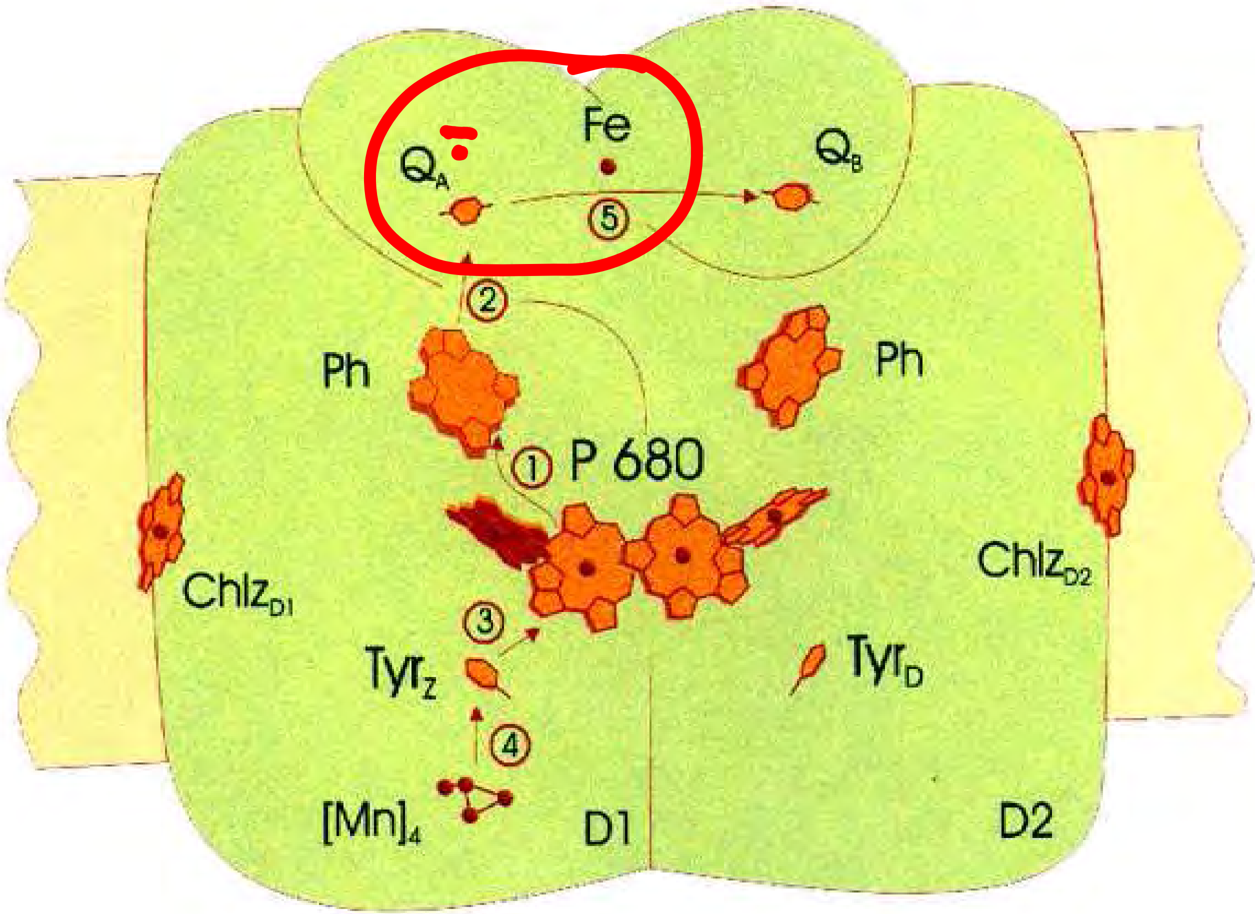
Photosystem II



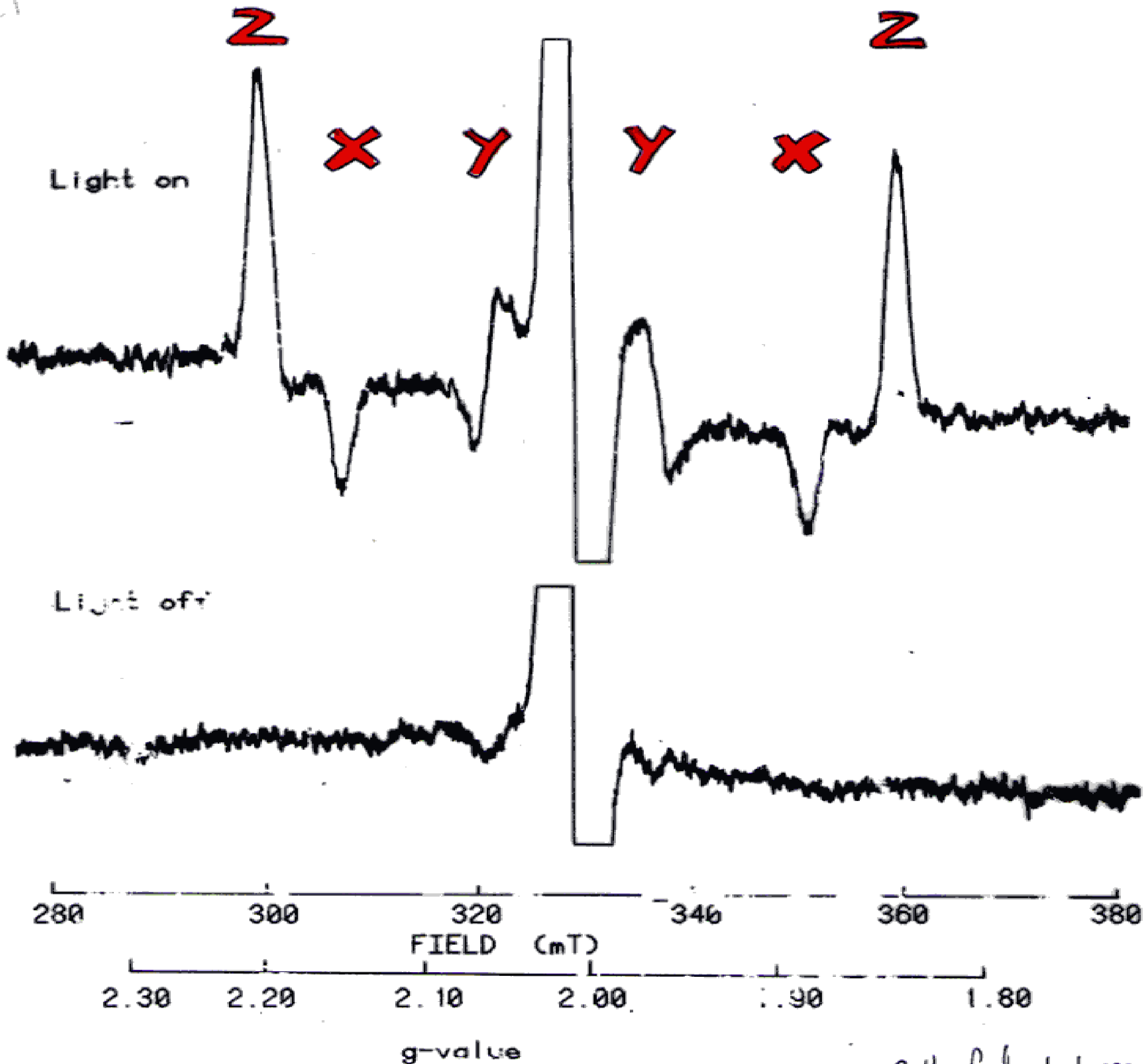


Rutherford et al 83
Rutherford & Zimmerman 84
see also Nugent et al '81

Photosystem II

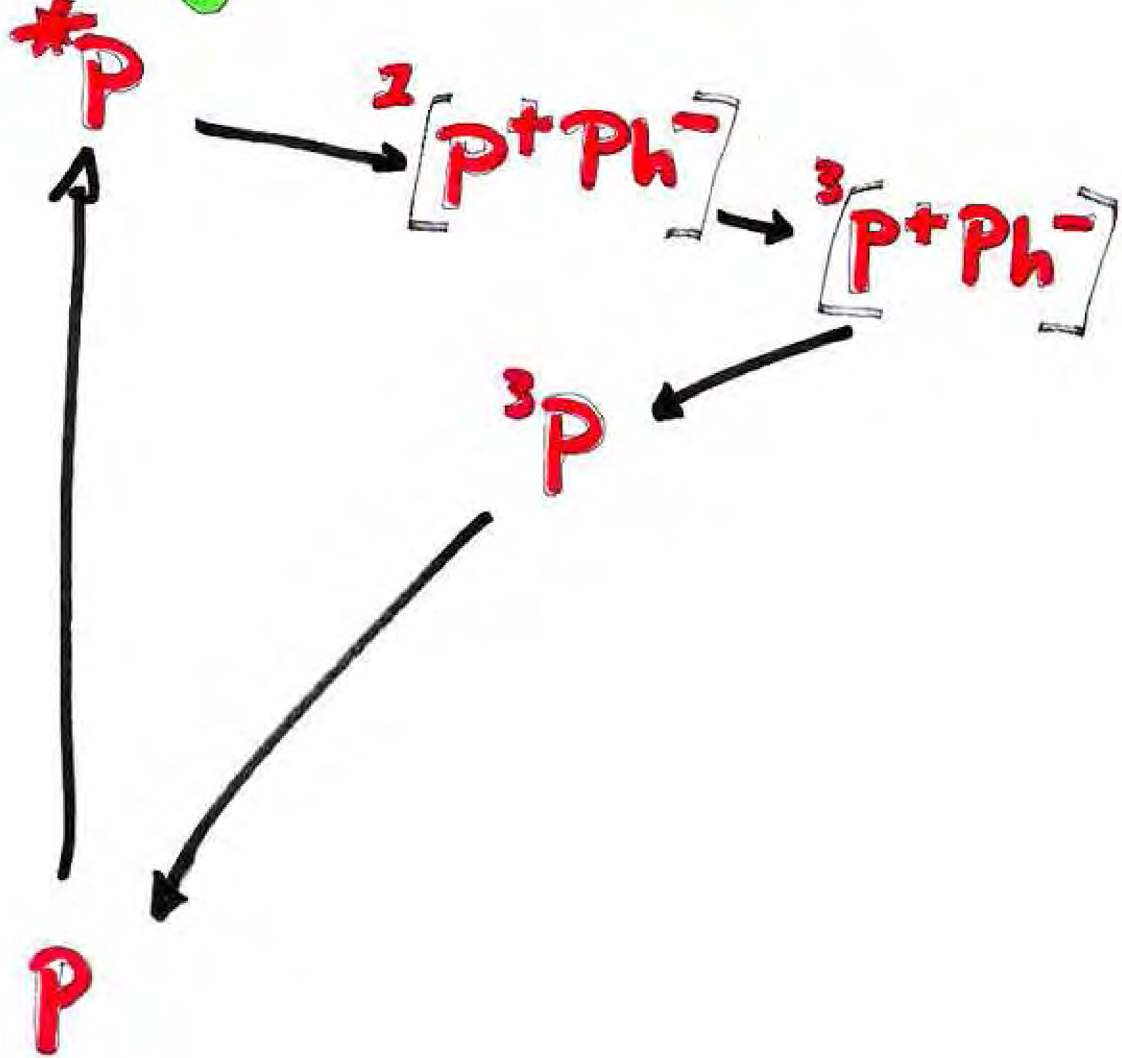


Reaction Centre triplet in PSII

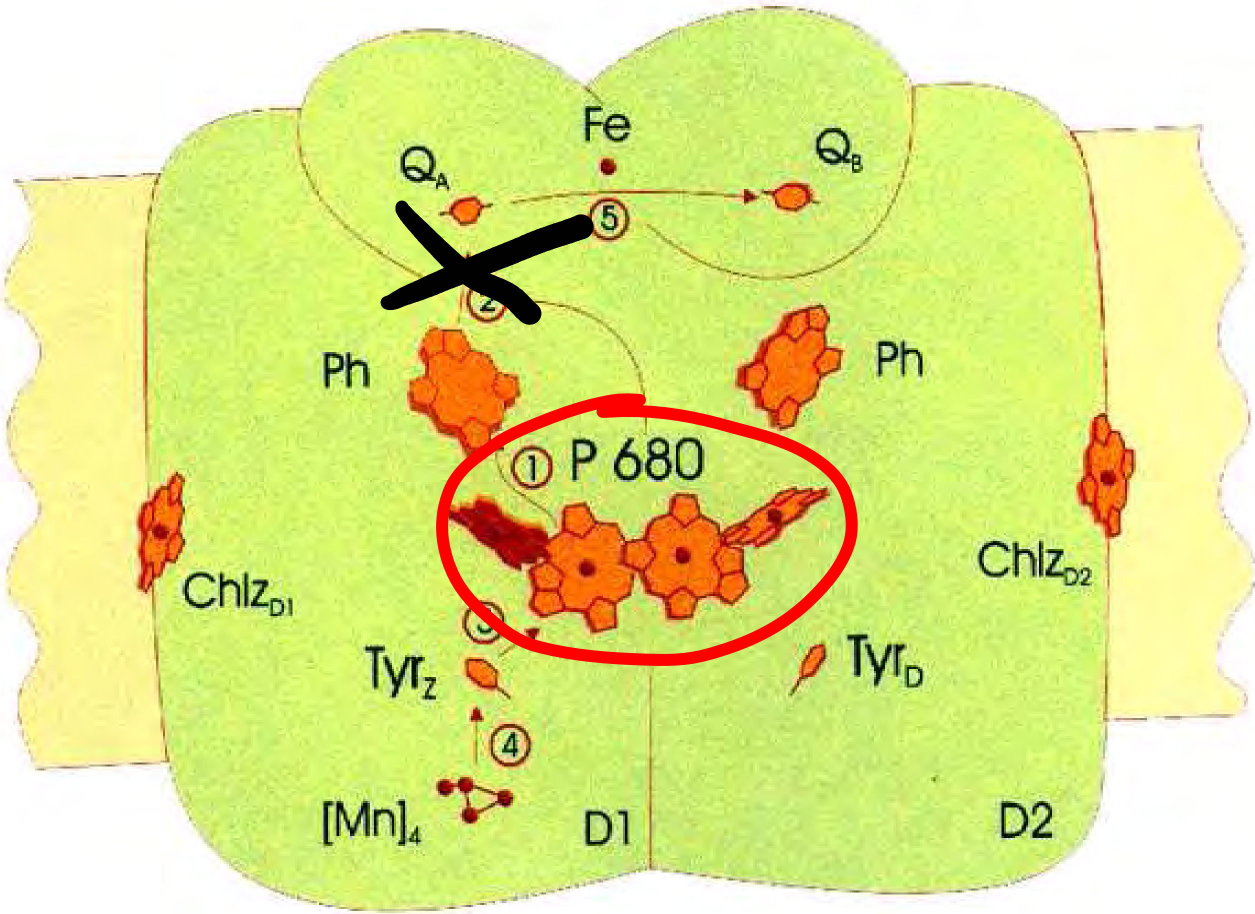


Rutherford et al 1981

Radical pair recombination triplet chlorophyll in PS II

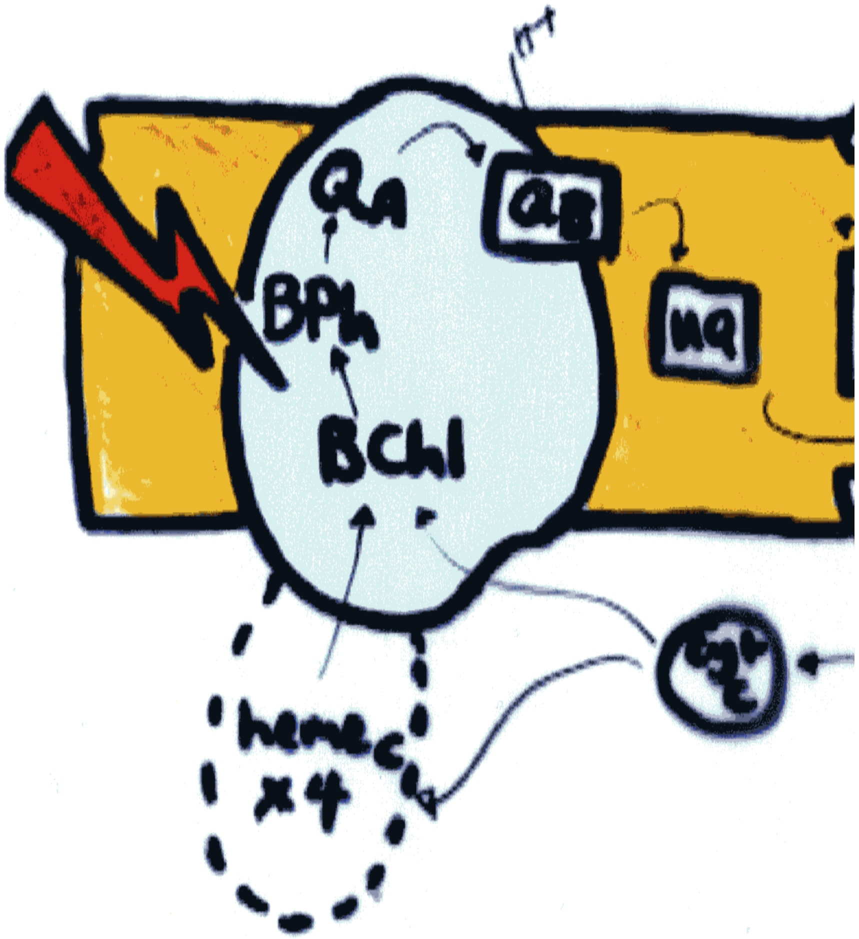


Photosystem II

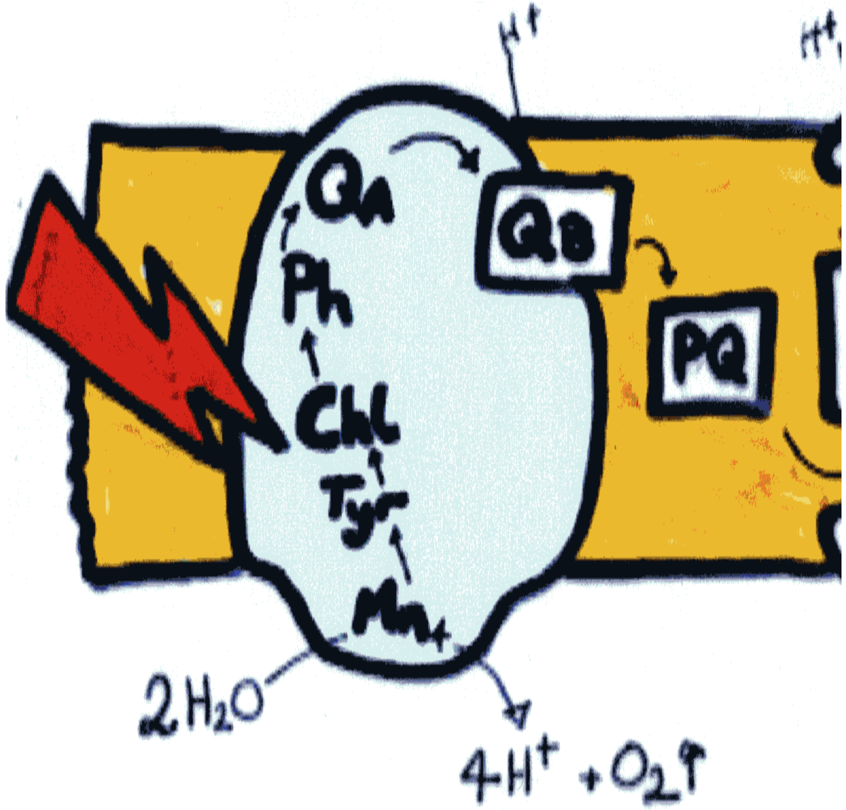


the water oxidizing enzyme

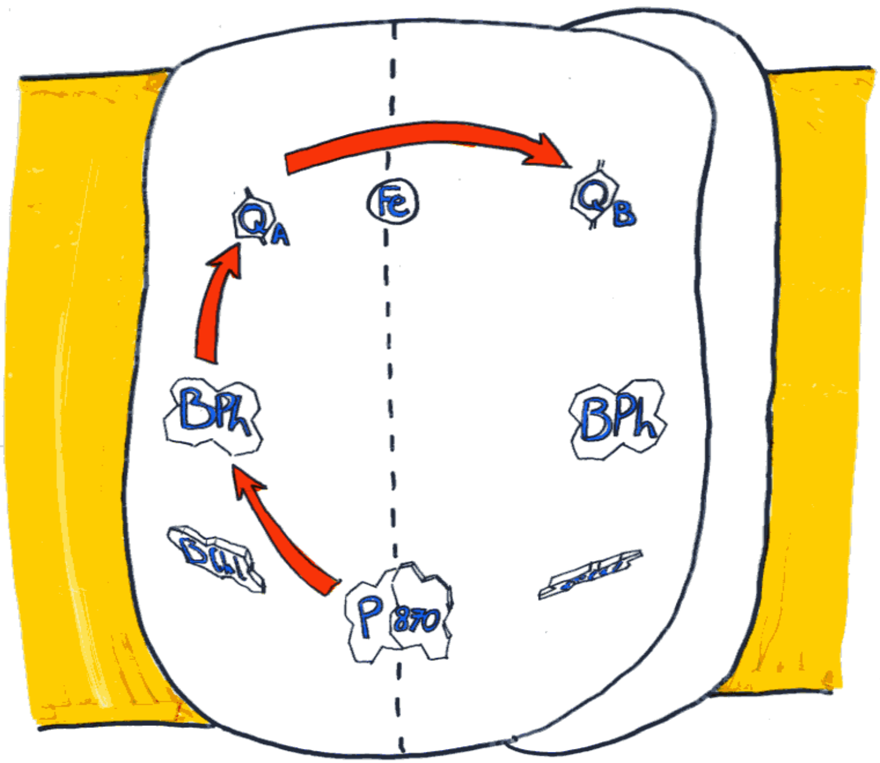
Purple bacteria



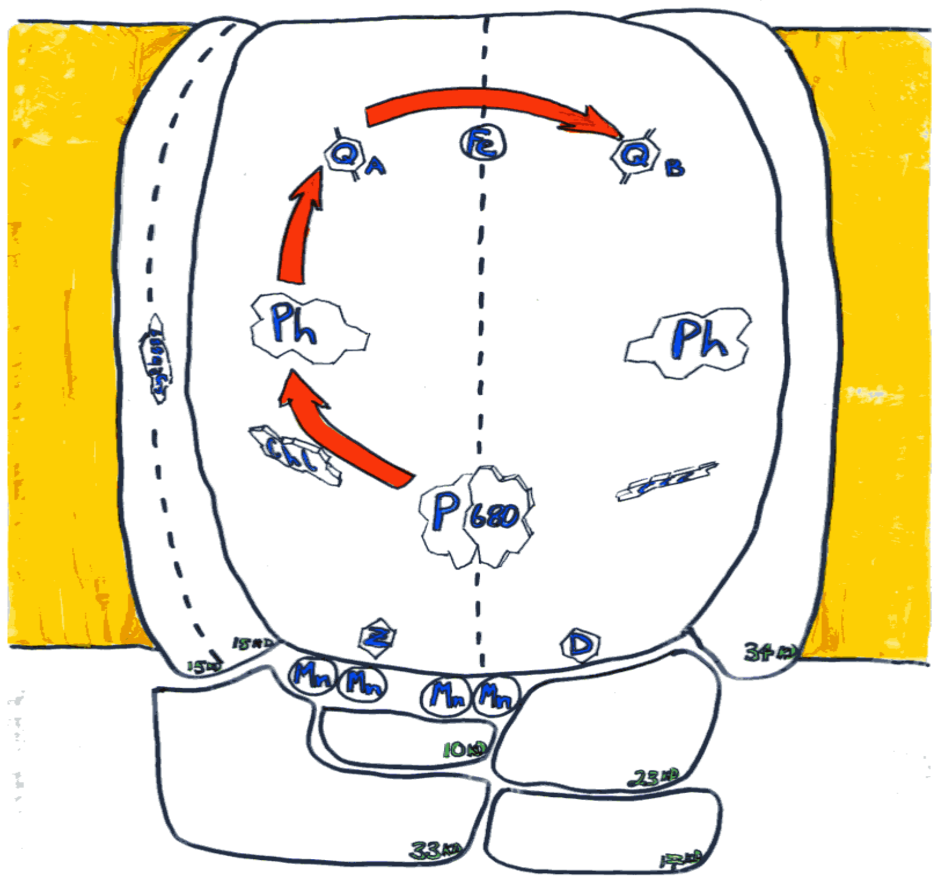
PSII



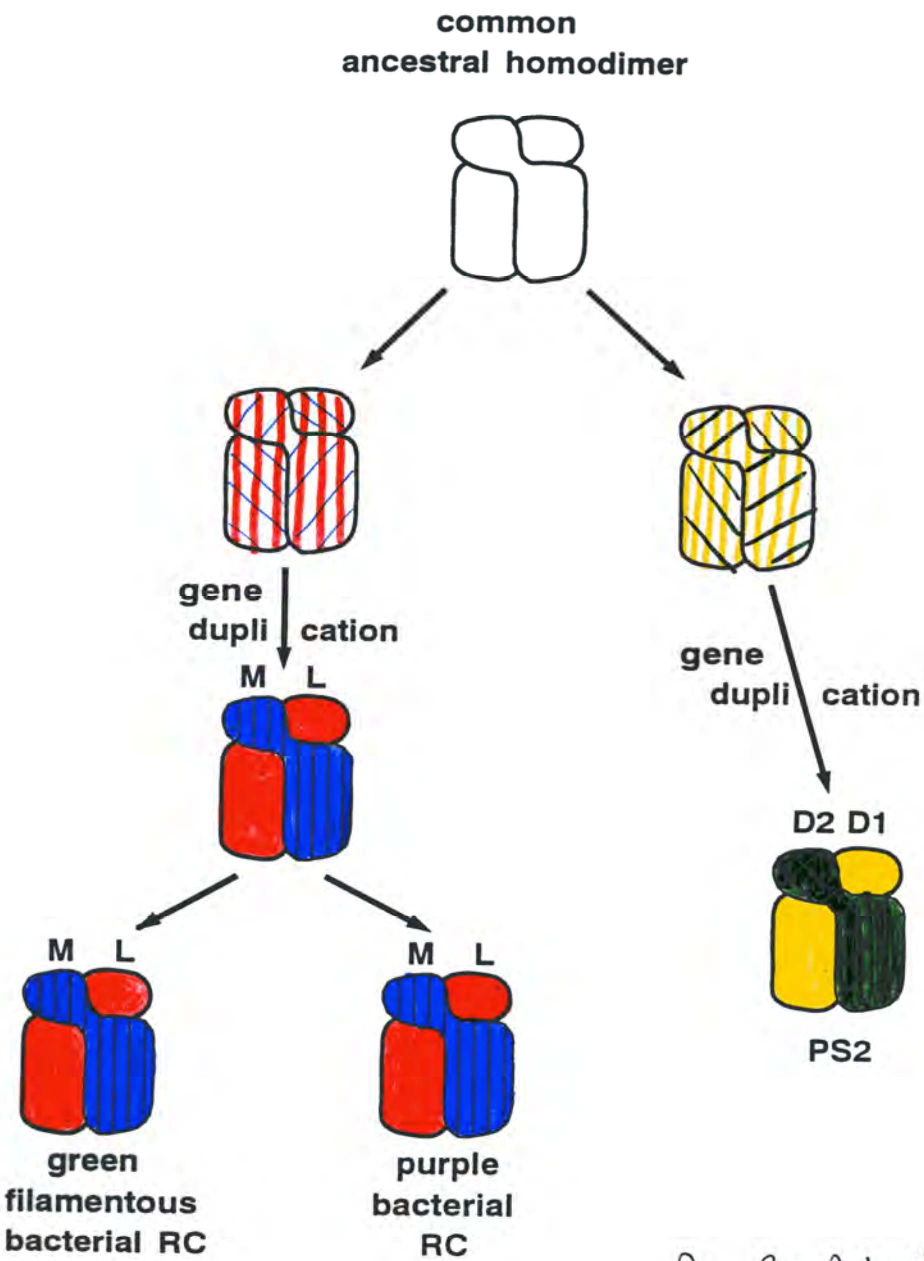
Purple bacteria



Photosystem II



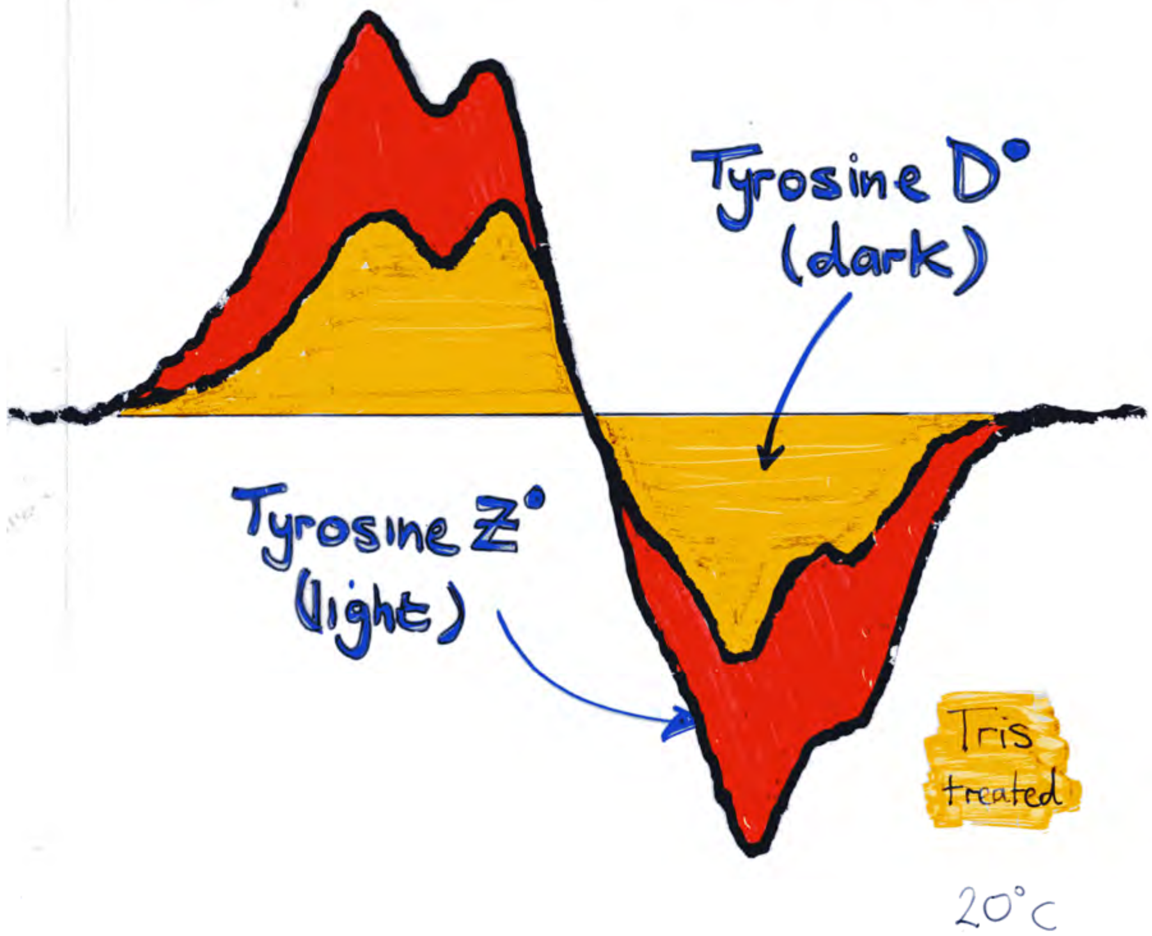
Rutherford 1985



From Rutherford & Nitschke 1994

see also Blankenship Beanland and others. but see Lockhart et al 1996

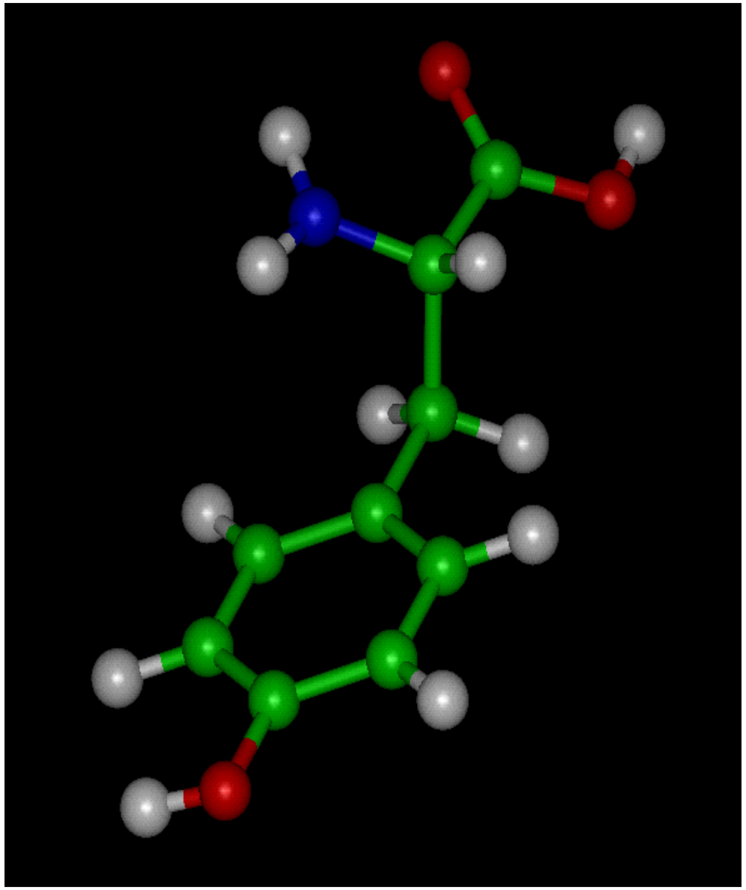
Tyr Z° is easily detectable when the Mn cluster is removed by a treatment with Tris

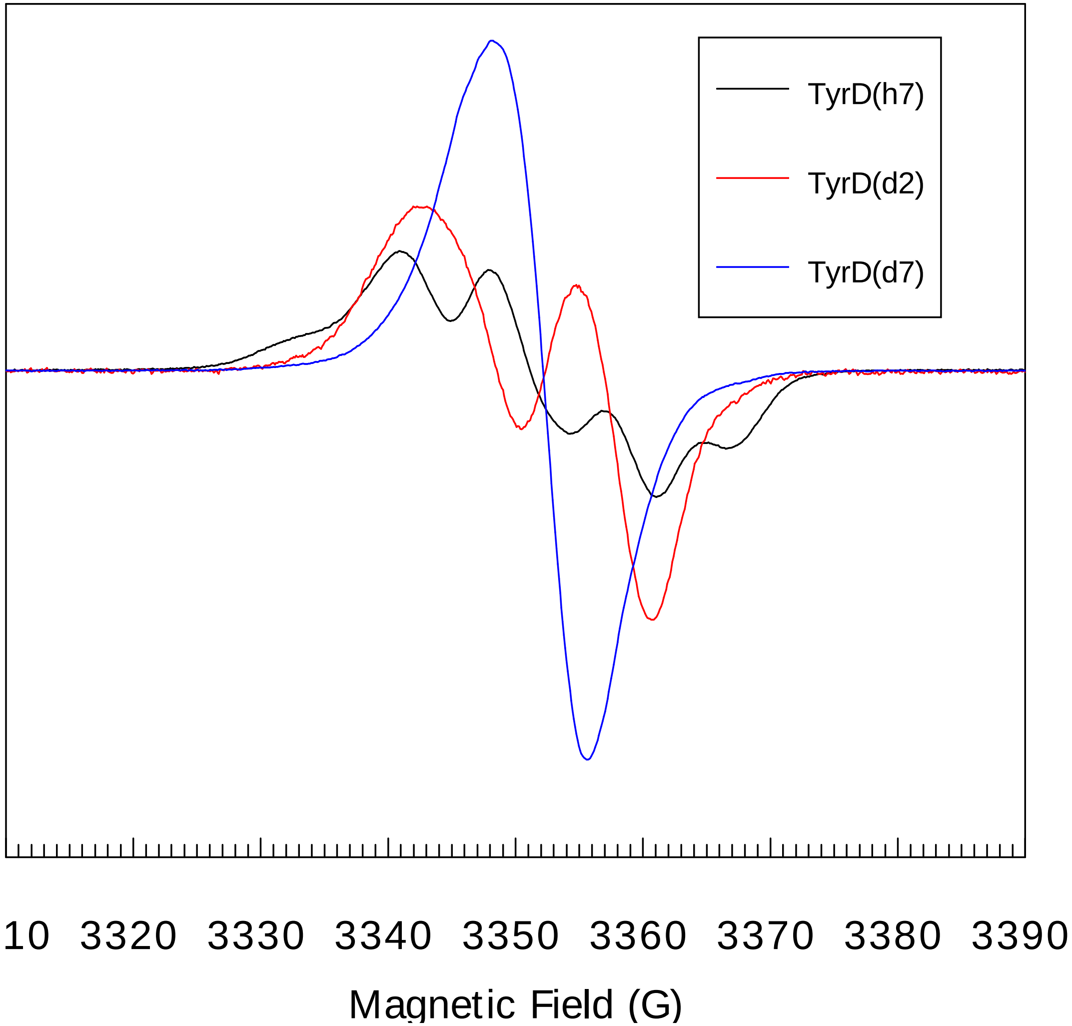


Tyrosyl radicals identified by isotopic labelling

Barry and Babcock 1987

these data done in T.elongatus by A. Boussac

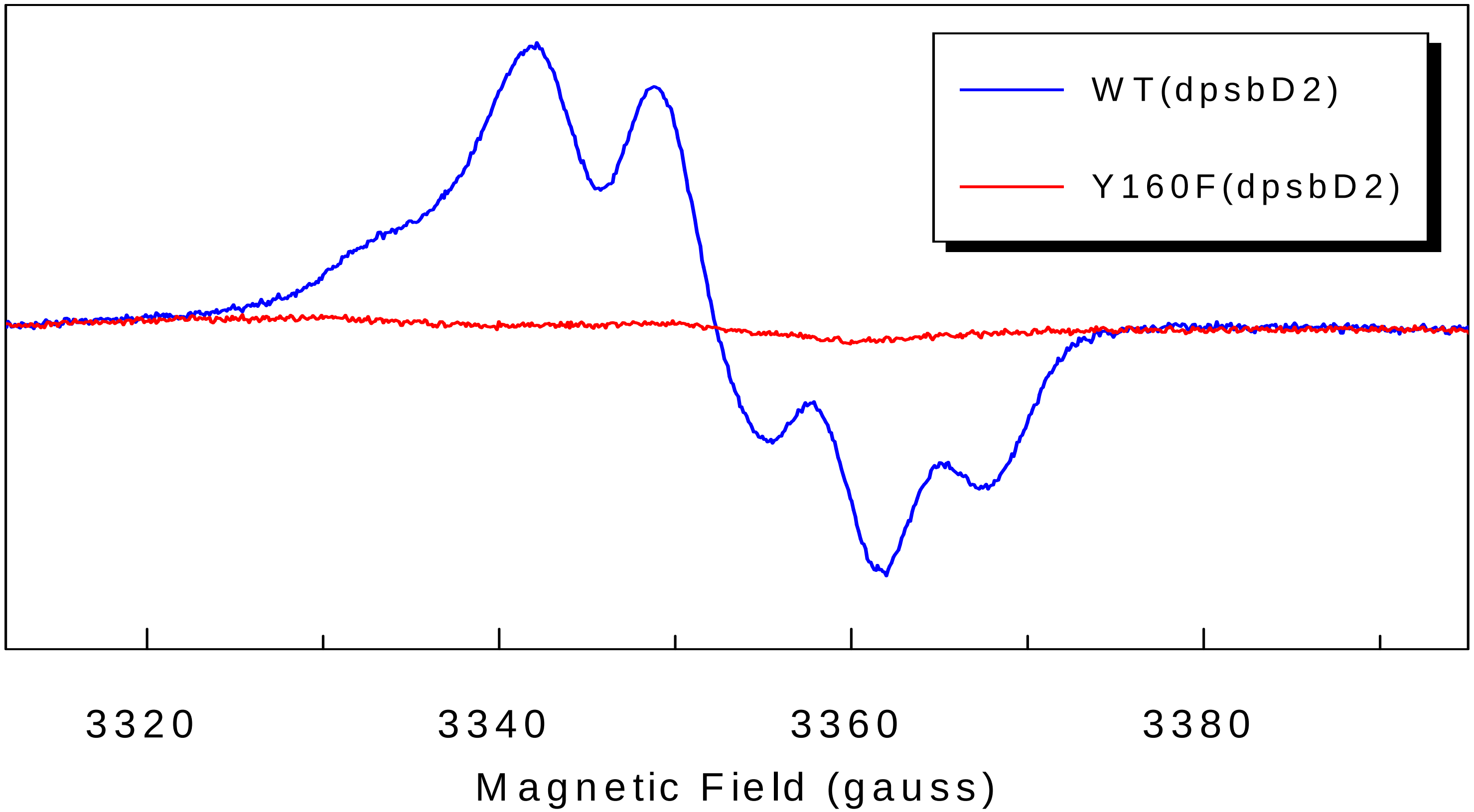




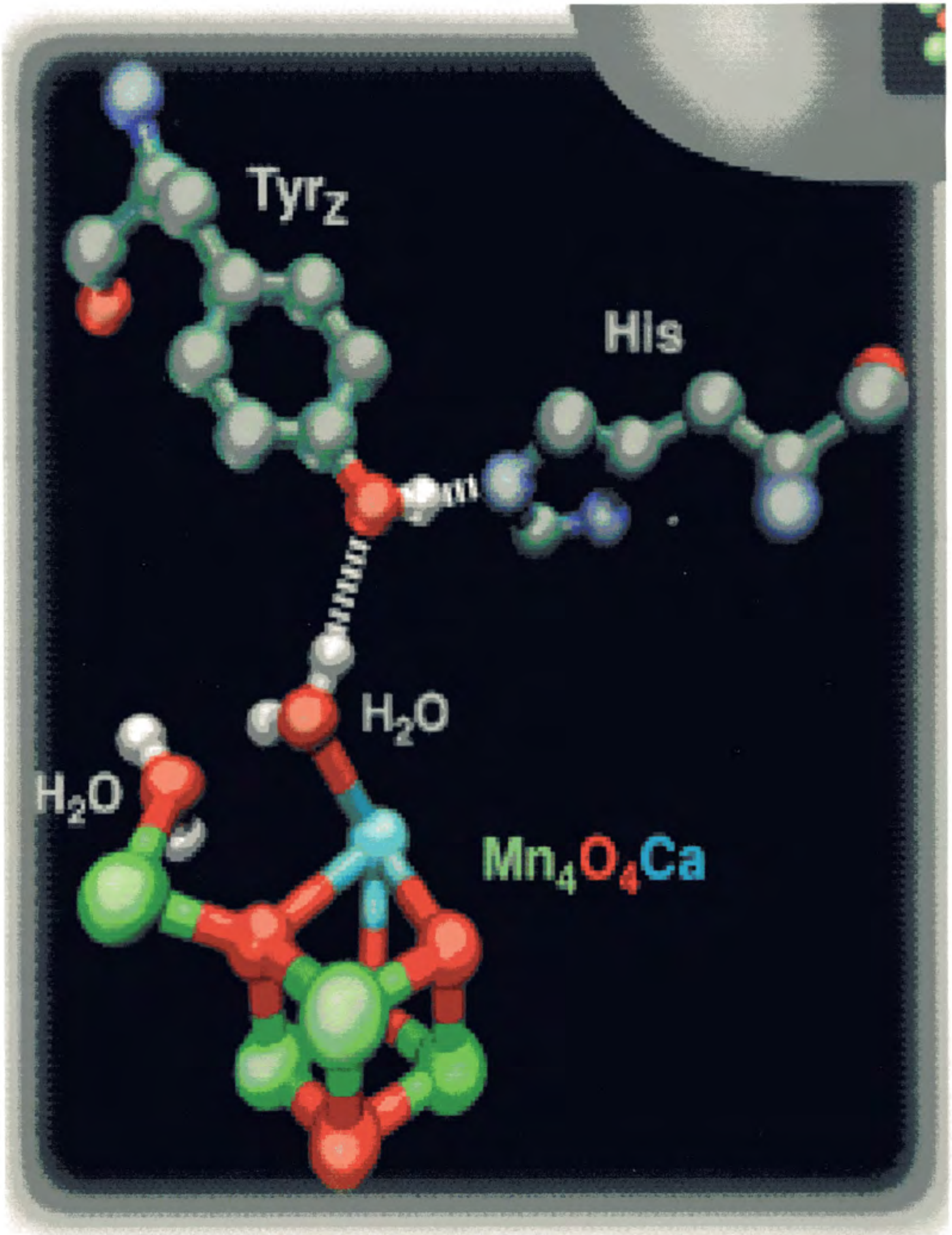
Tyrosyl radicals identified and localized by site-directed mutagenesis

Vermaas et al 1988

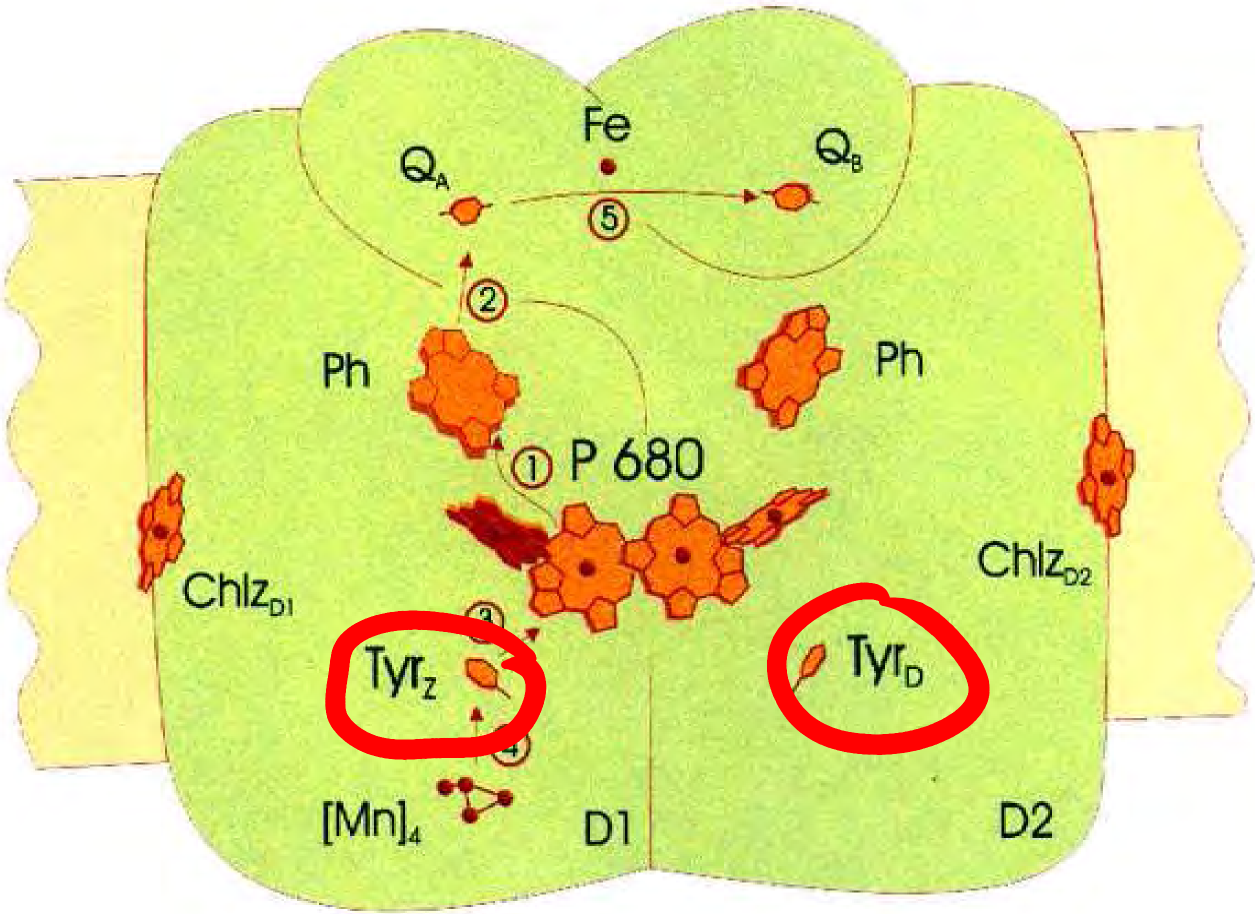
Debus et al 1988



these data from T.elongatus from Sugiura et al 2004

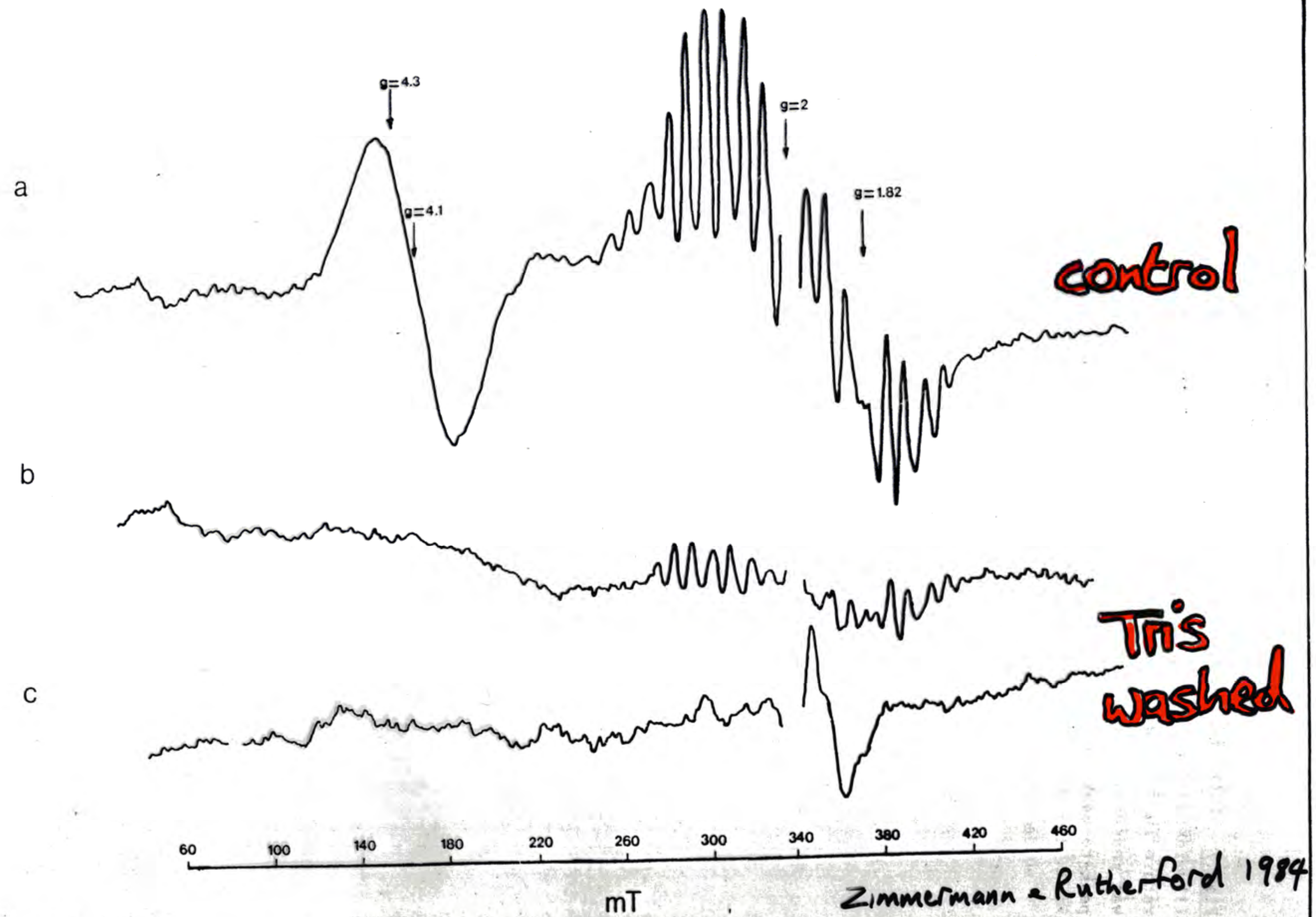

Tyr$_Z$
His
H_2O
H_2O
Mn_4O_4Ca

Photosystem II



the water oxidizing enzyme

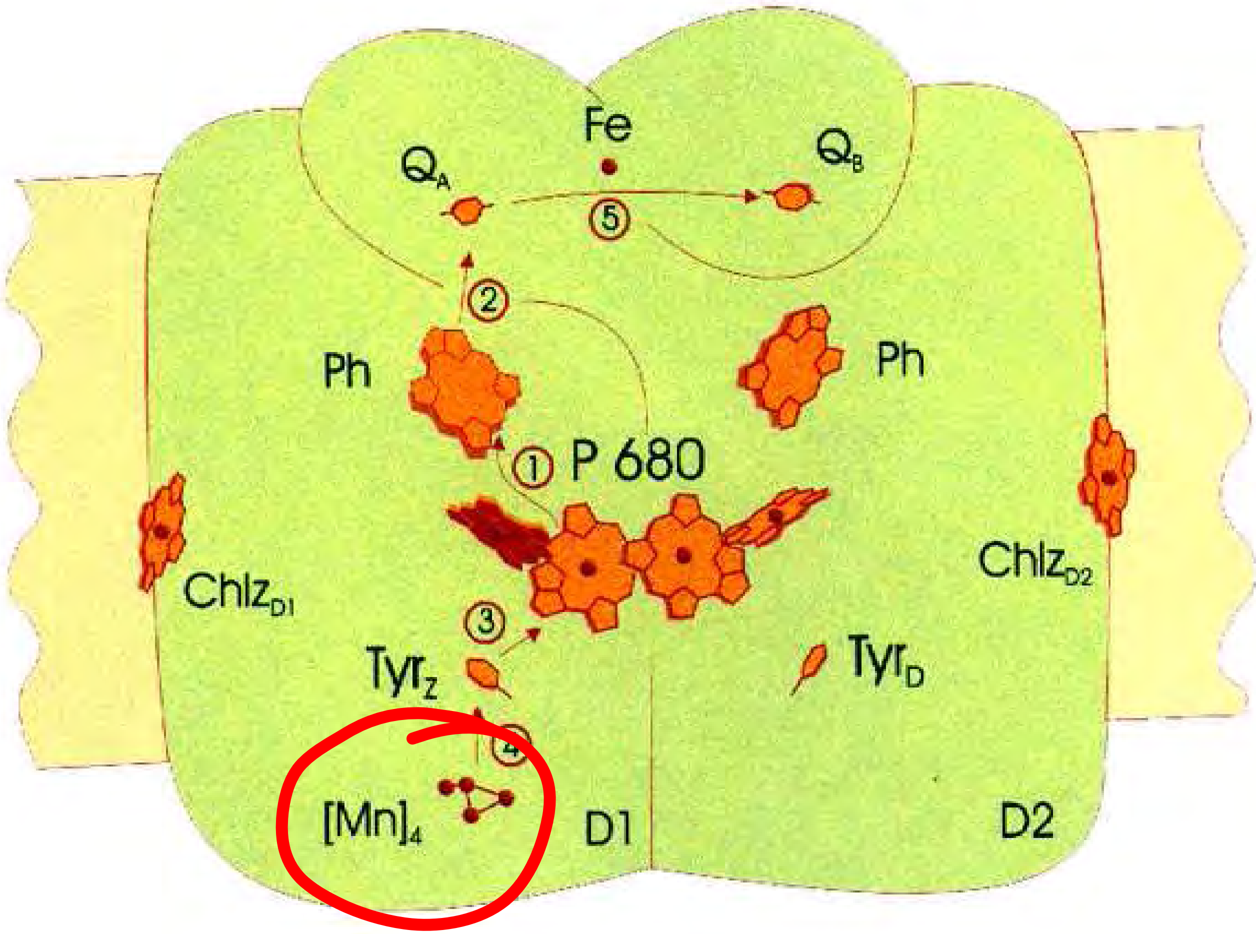
2 signals are formed by illumination at 200K



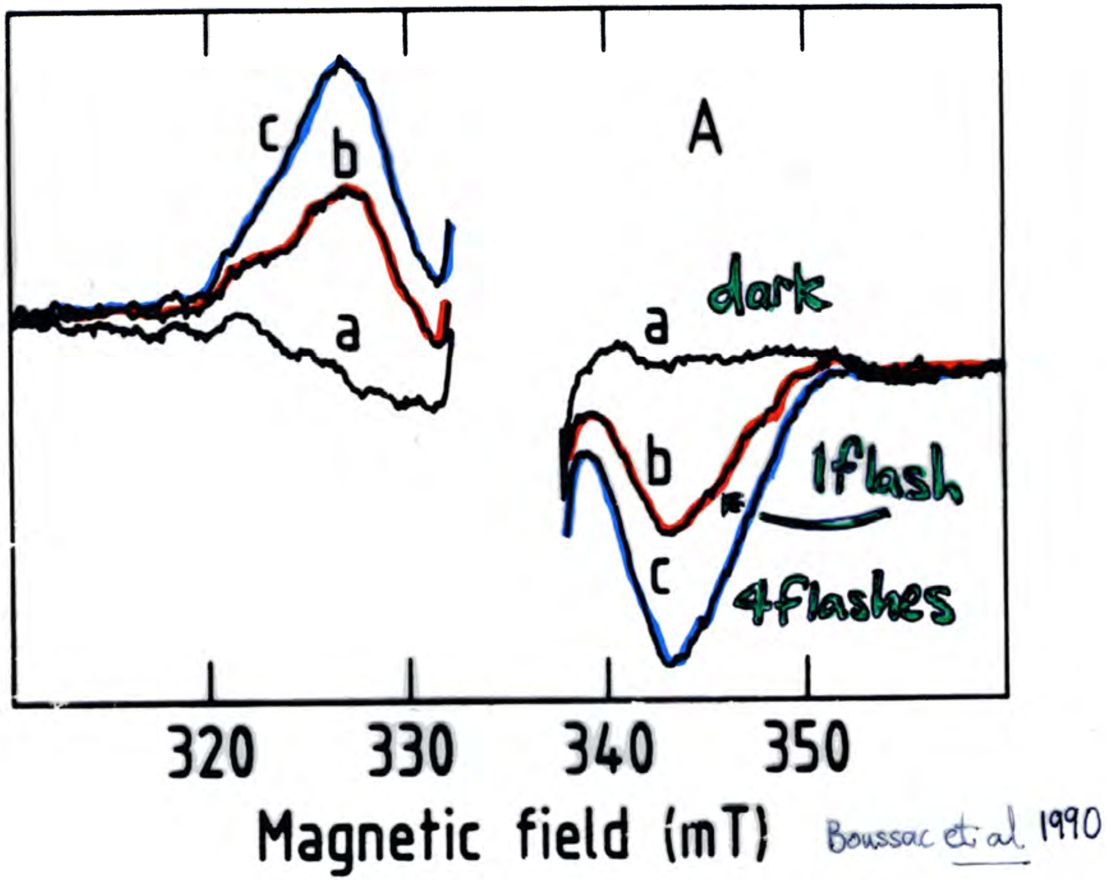
Zimmermann & Rutherford 1984

Fig 1

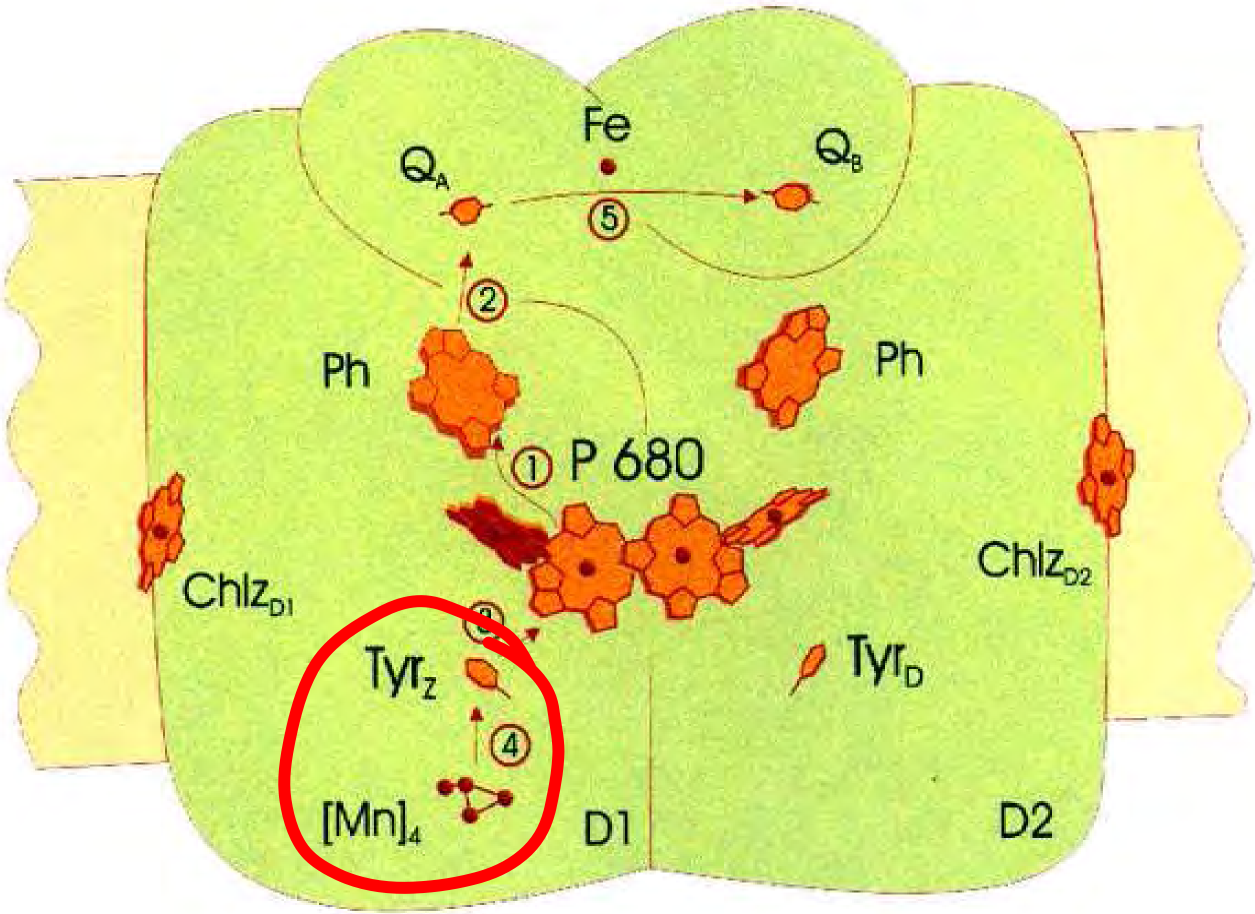
Photosystem II



The ~~S3~~ $S_2Tyr_Z^{\cdot}$ signal is formed with a high yield upon flash illumination



Photosystem II

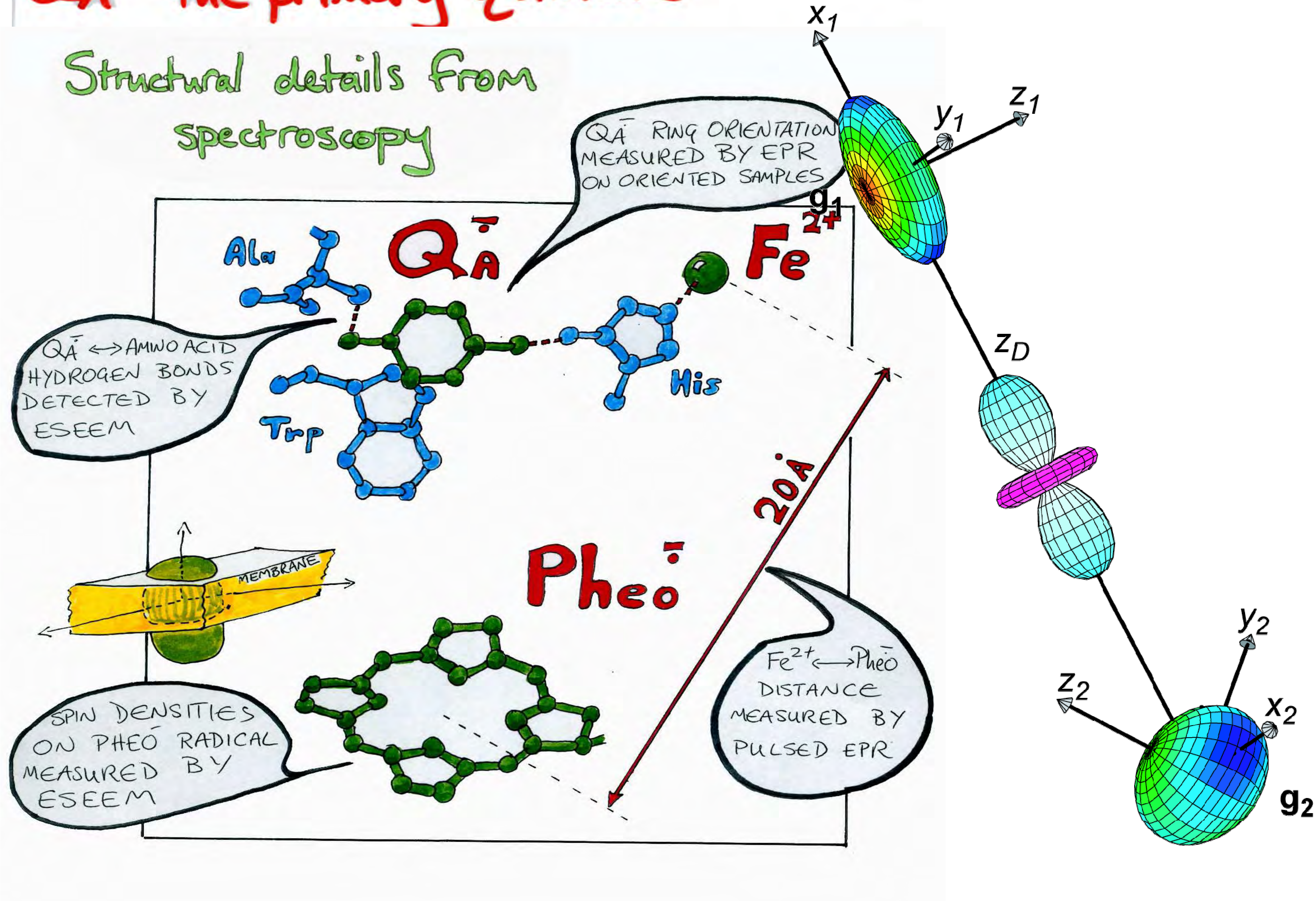


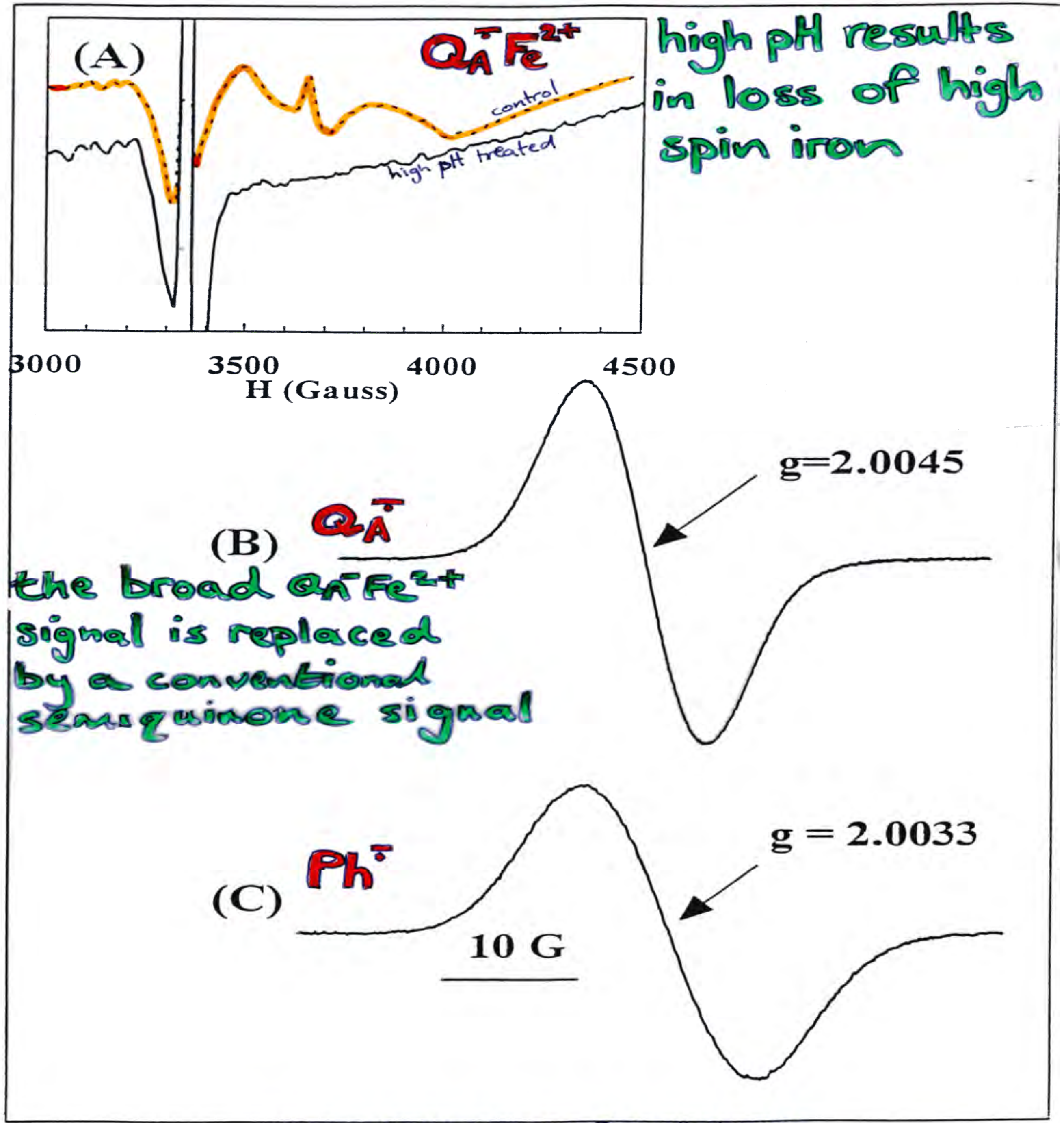
Phase 2

structural studies using EPR

EPR of the quinones in PSII

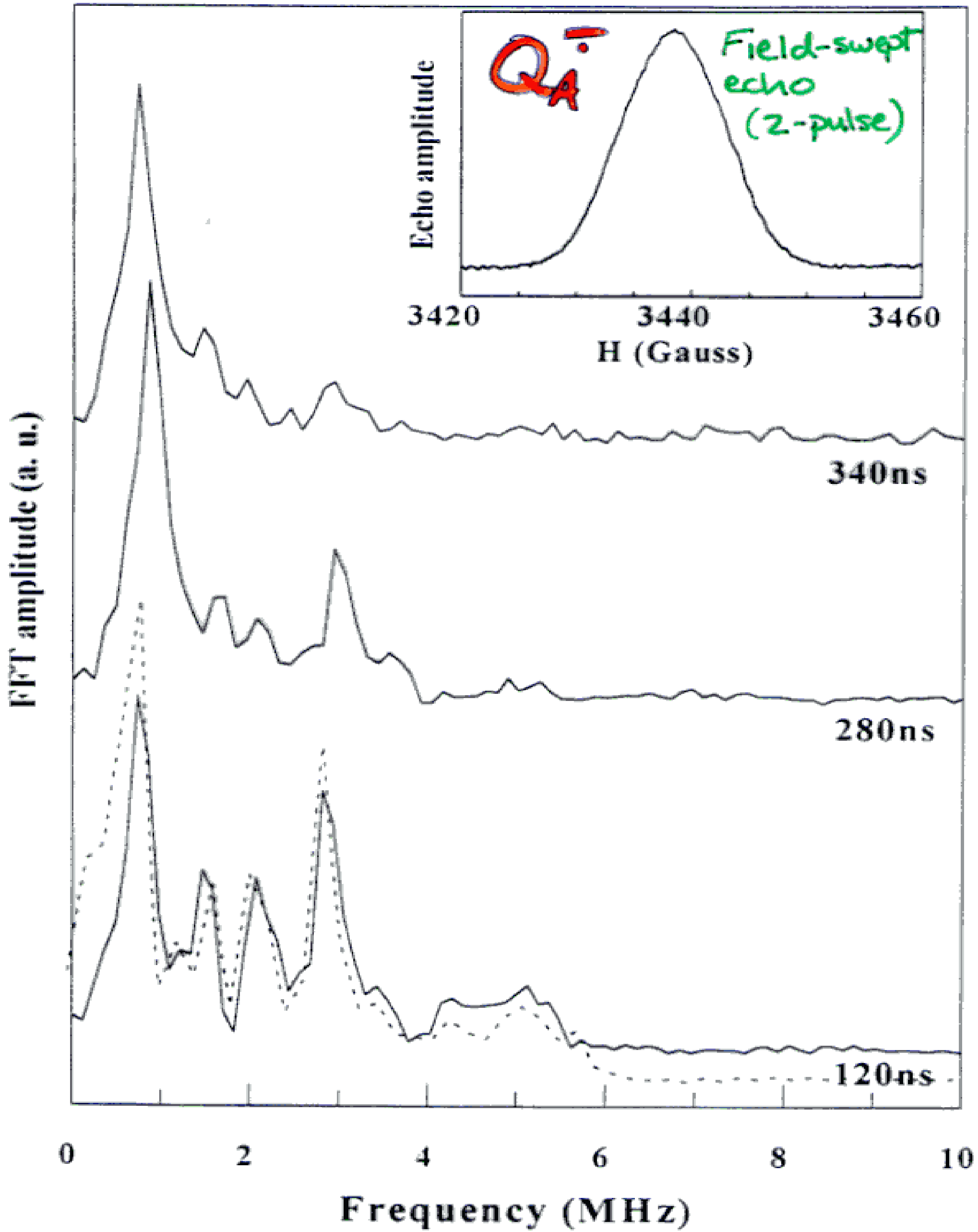
Q_A^{-} the primary quinone



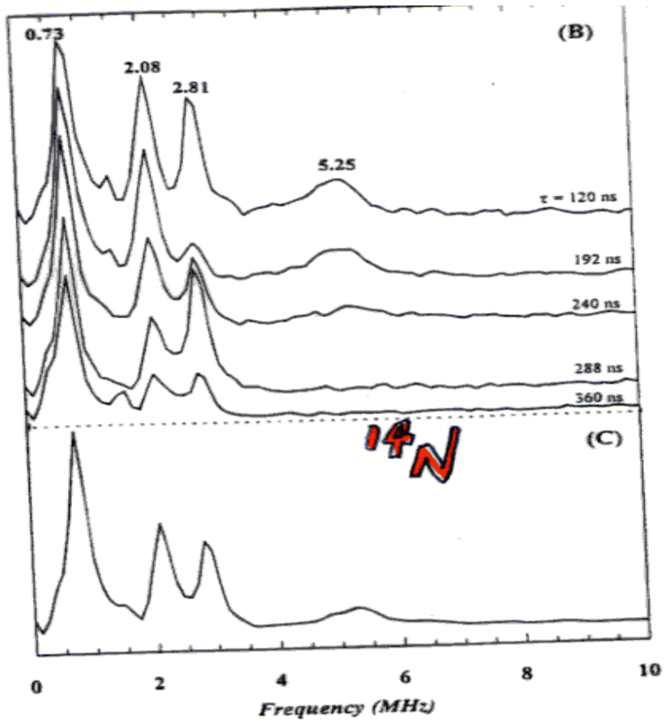


Deligiannakis, Jegerschold e Rutherford 1997

FT 3pulse ESEEM of Q_A^- in PSII pre-treated at high pH

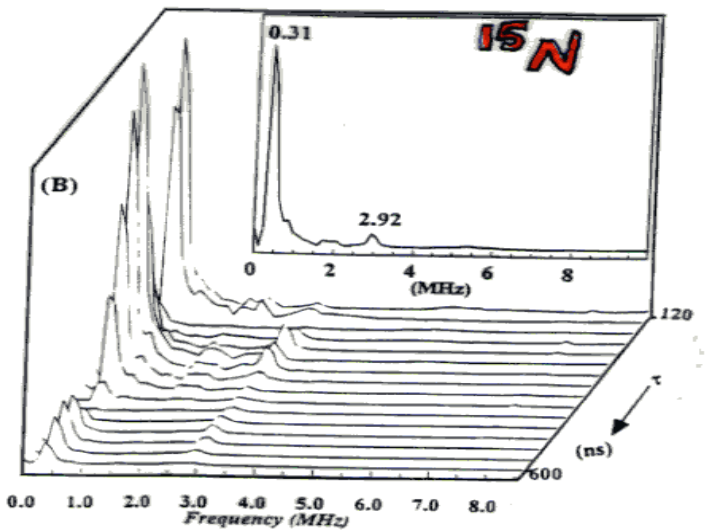


The couplings detected by ESEEM in Q_A^- of PSII arise from nearby nitrogen nuclei



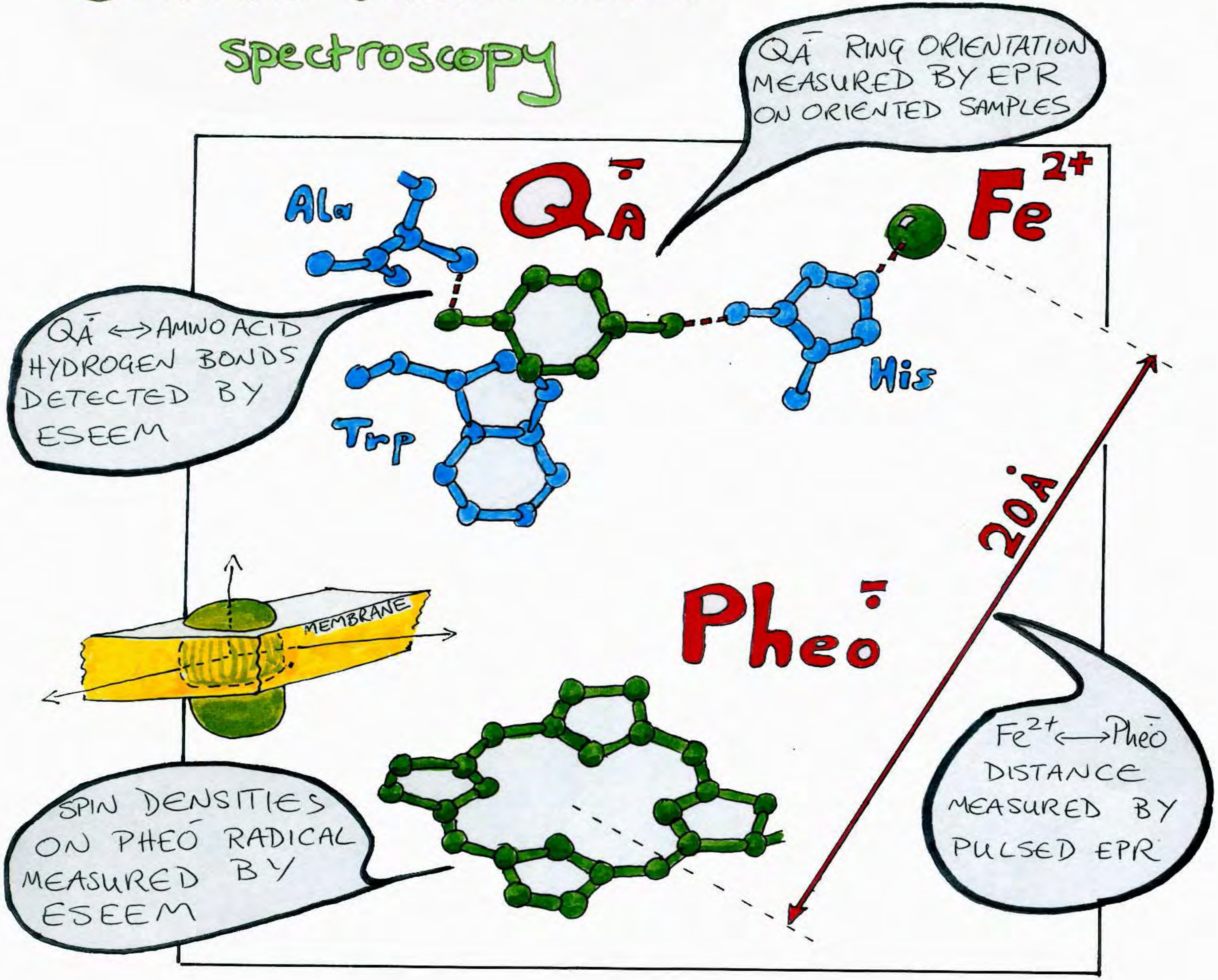
sample:

Mn depleted PS II treated with cyanide to convert Fe^{2+} to low spin. Dithionite added to form semiquinone.

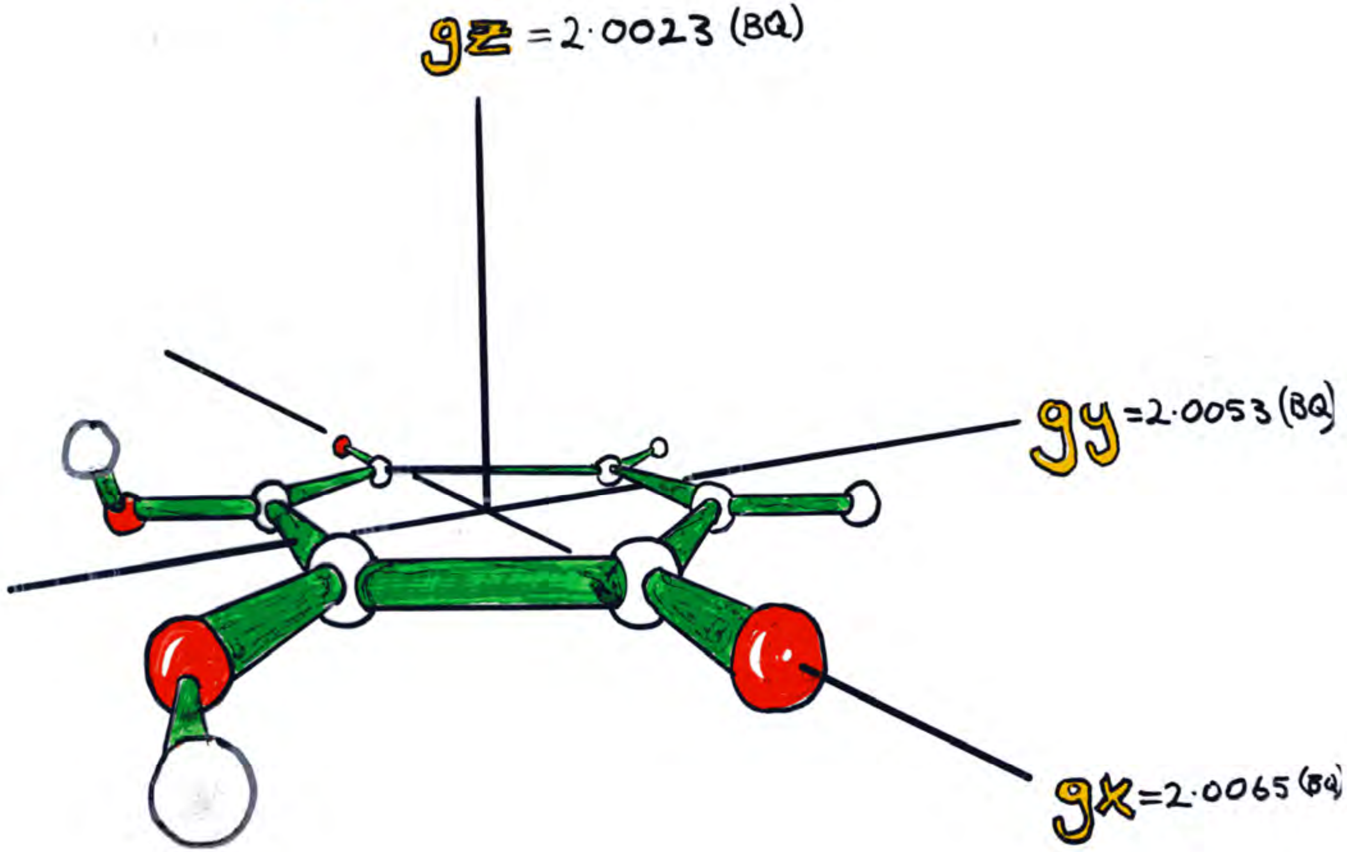


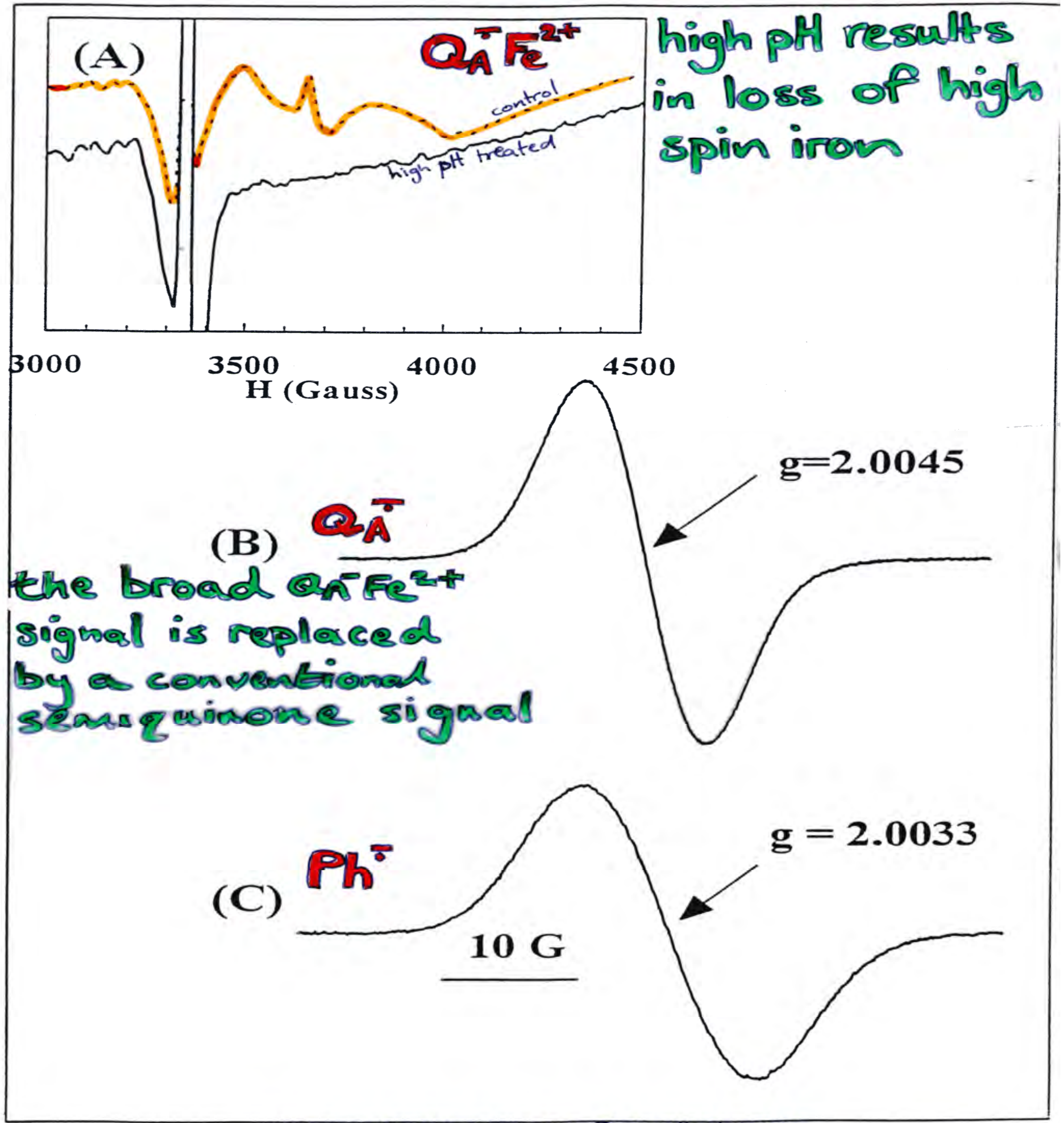
Deligiannakis Boussac & Rutherford (1995)

Structural details from spectroscopy



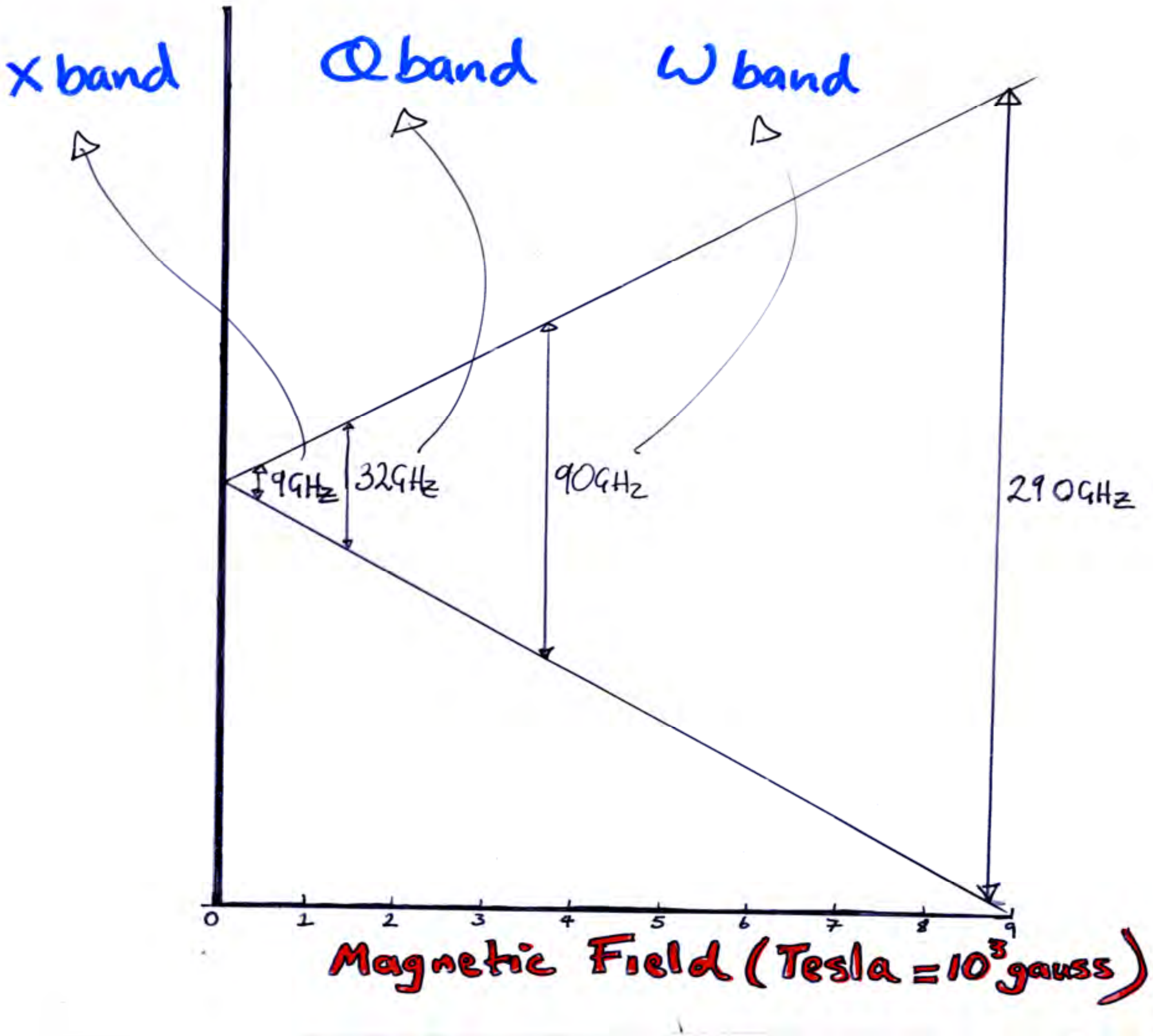
Ubiquinone



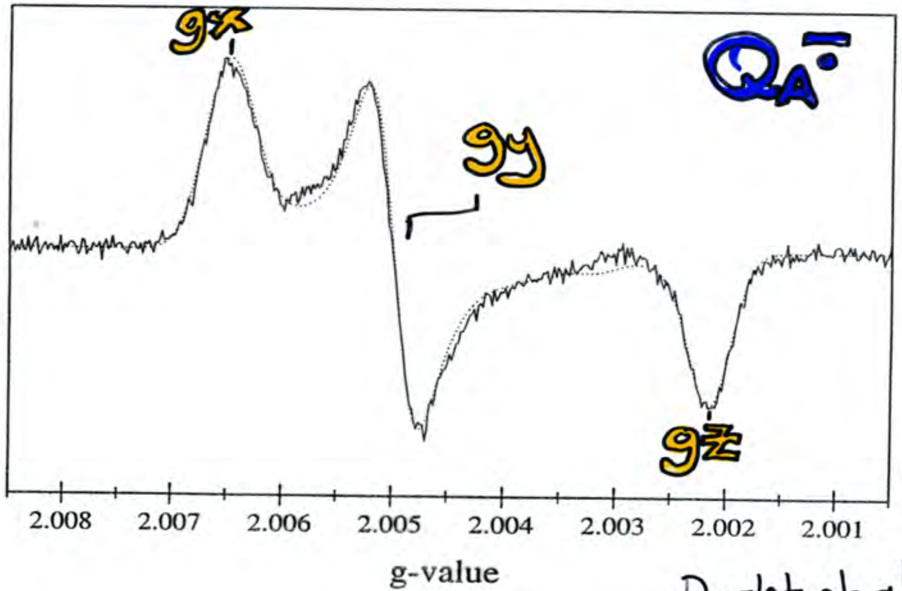


Deligiannakis, Jegerschold & Rutherford 1997

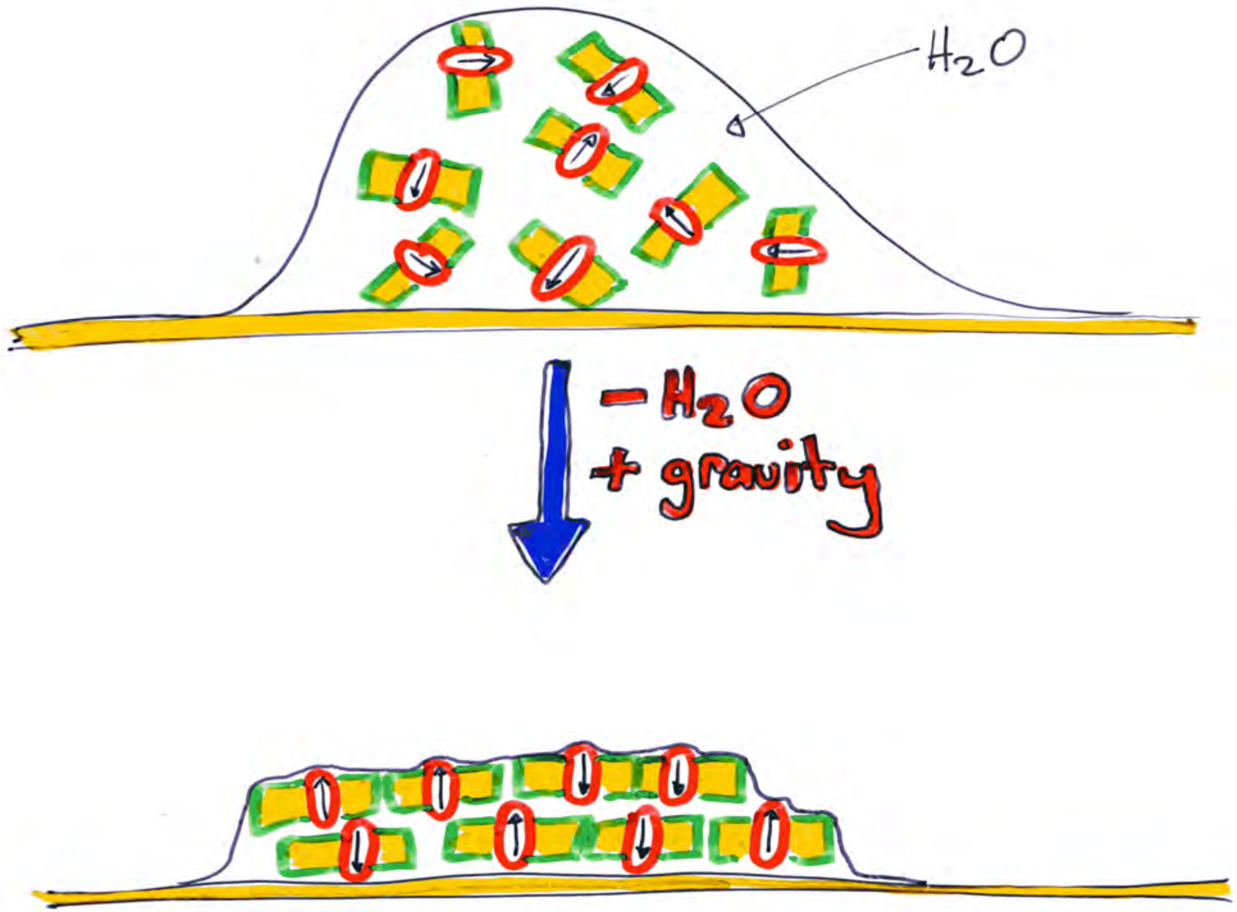
High field, 290GHz EPR



High Field EPR spectrum of Q_A in PSII

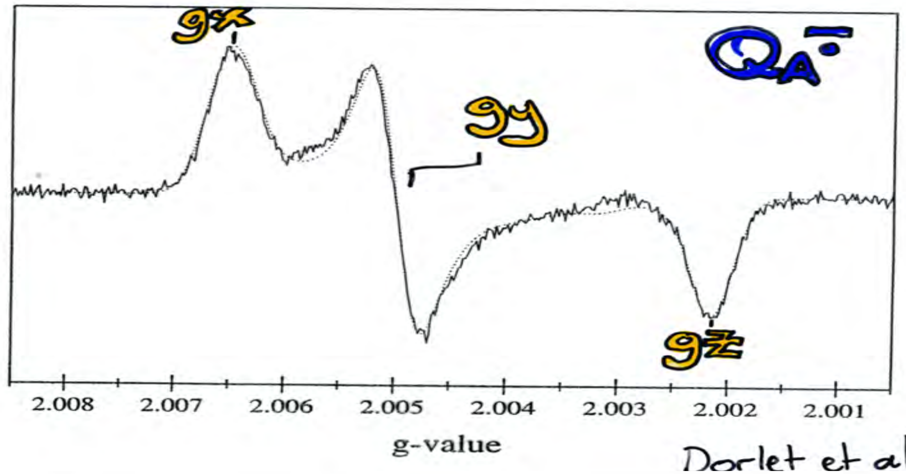


Dorlet et al (2000)

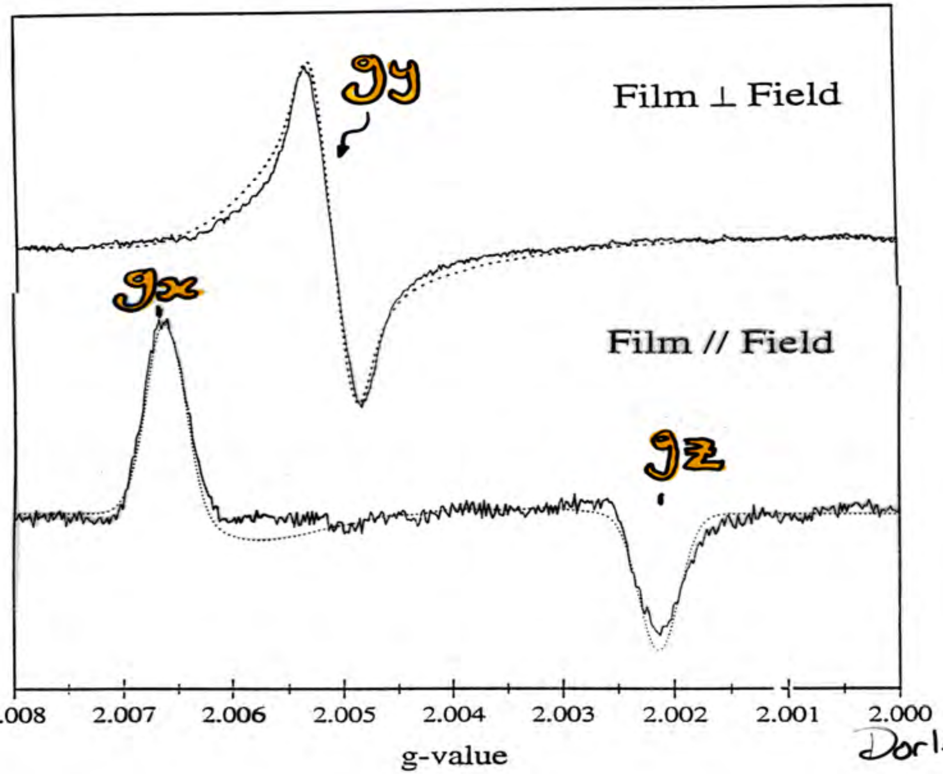


1-dimensionally ordered multilayers of membranes

High Field EPR spectrum of Q_A in PSII

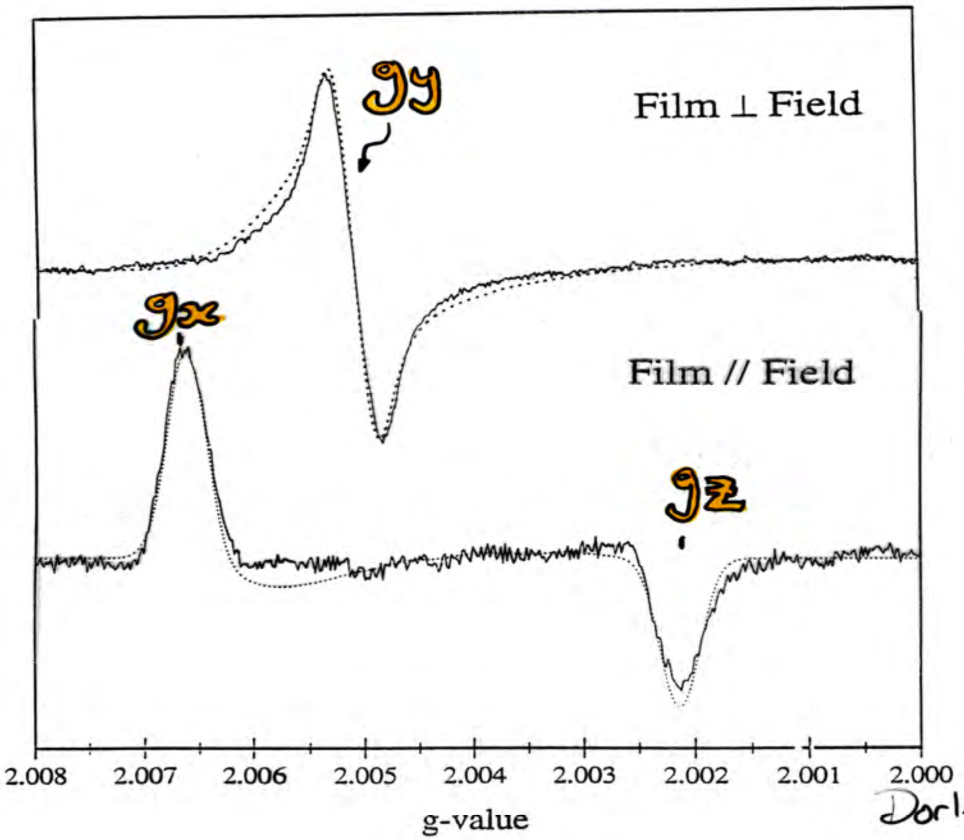


Dorlet et al (2000)

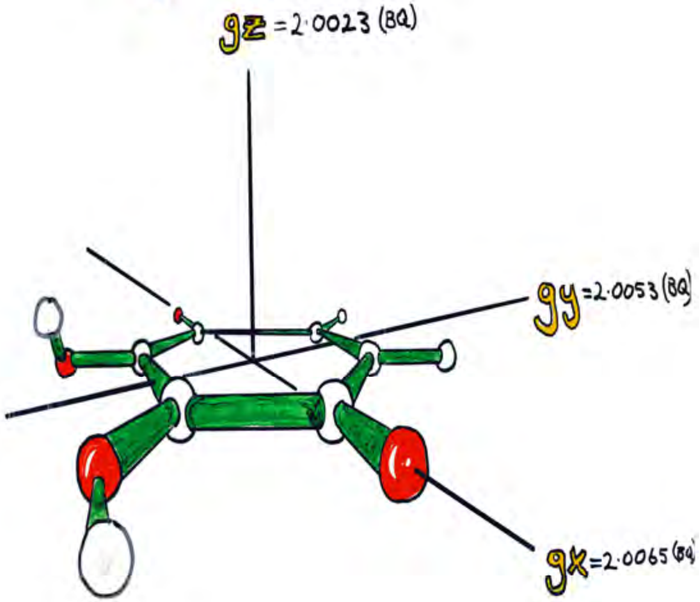


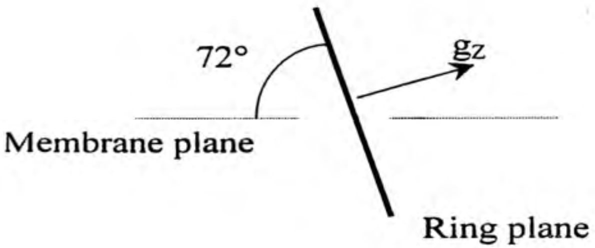
Dorlet etal (2000)

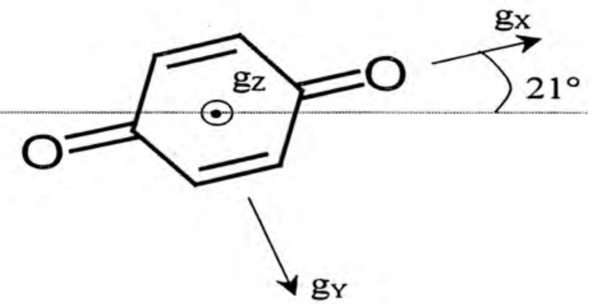
Ubiquinone



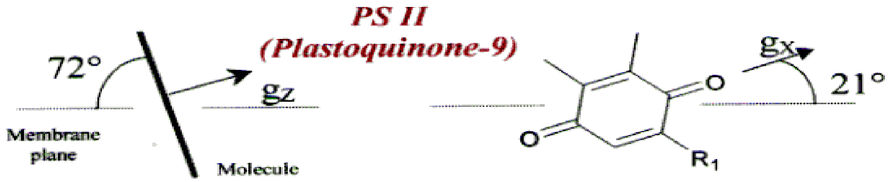
Dorlet et al (2000)





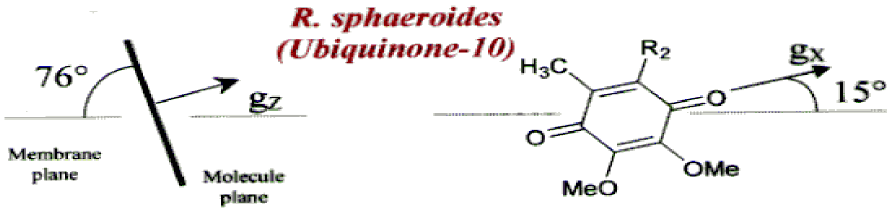


Angular Orientation of Semiquinones in Photosynthetic Reaction Centers

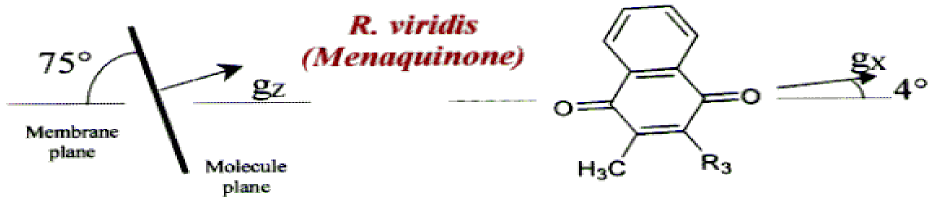


Dorlet, P., Rutherford, A. W., Un, S. (2000) Biochemistry 39, 7826.

MacMillan, F., Hanley, J., van der Weerd, L., Knüpling, M., Un, S., Rutherford, A. W. (1997) Biochemistry 36, 9297.

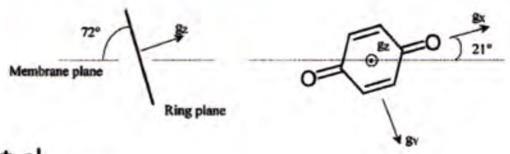


Yeates, T. O., Komiya, H., Chirino, A., Rees, D. C., Allen, J. P., Feher. G. (1993) PDB code 4RCR

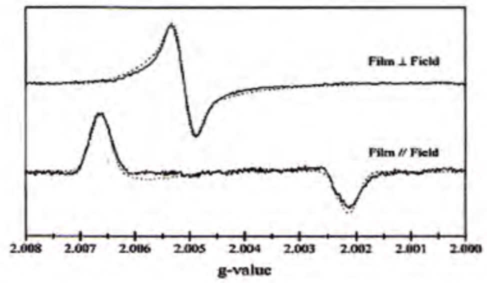


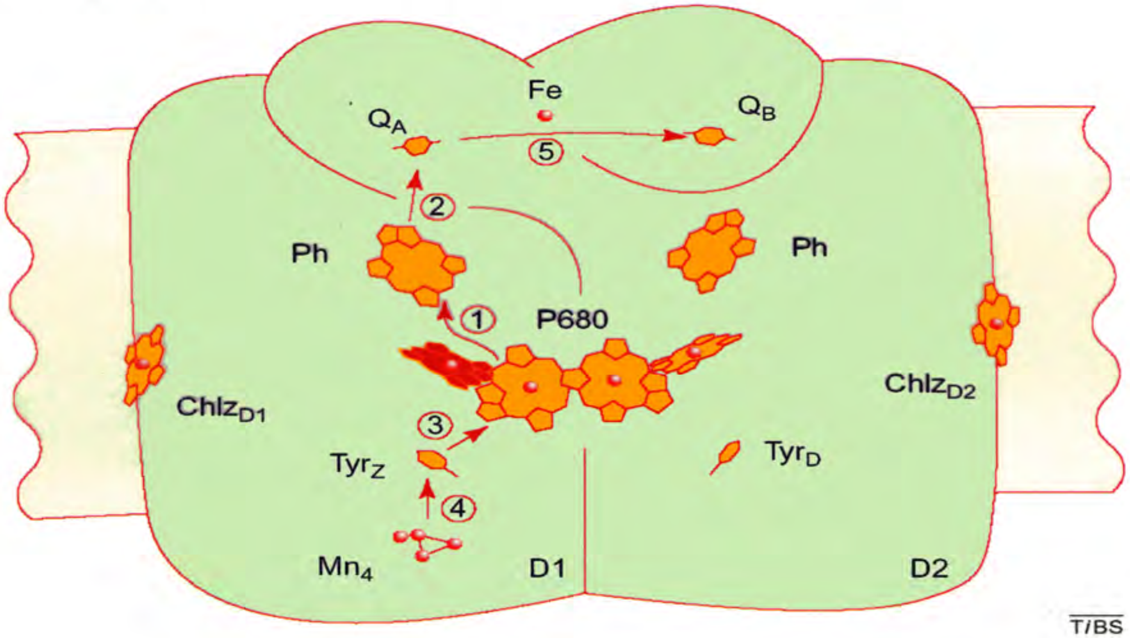
Deisenhofer, J., Epp. O., Sinning, I., Michel, H. (1994) PDB code 1PRC (revised 1PRCC)

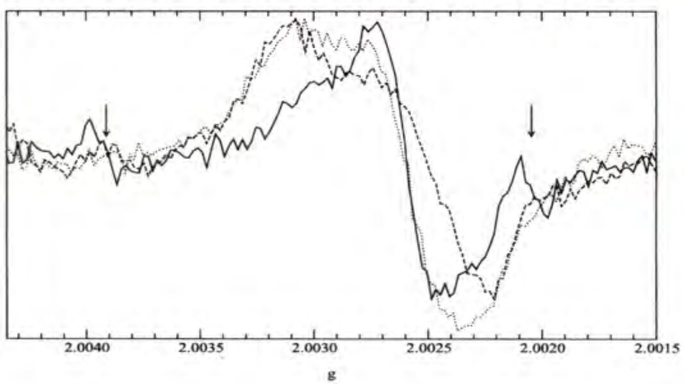
$Q_A^{\bullet -}$ orientation from 285 GHz-EPR data



Dorlet et al.
Biochemistry 2000

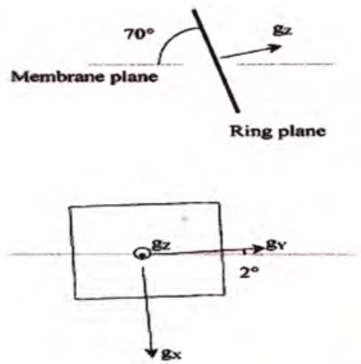


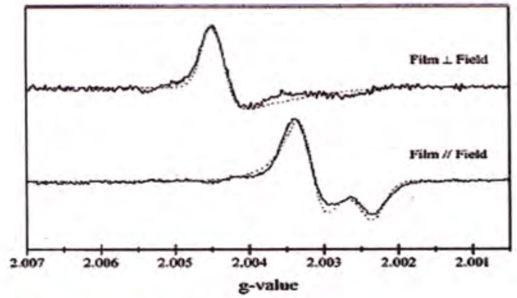




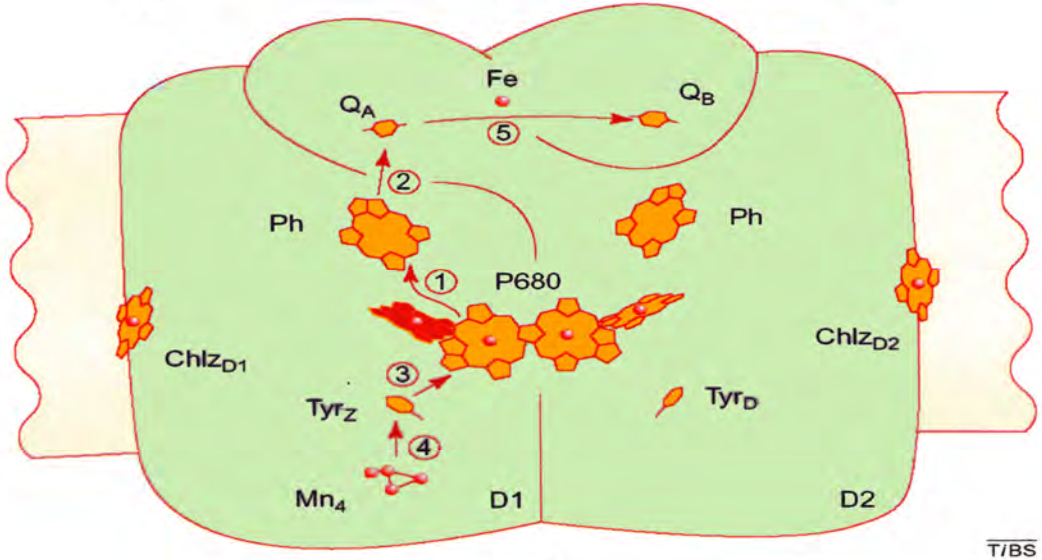
$Chl_Z^{\bullet +}$ orientation from 285 GHz-EPR data

Faller et al.
J. Phys. Chem. 2000

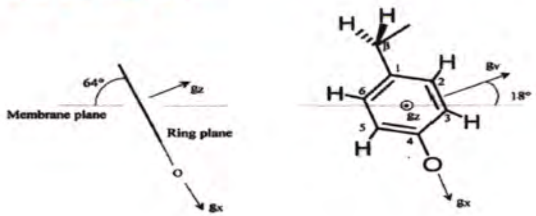


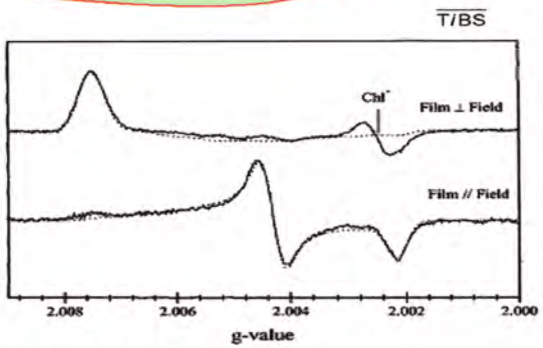


$Pheo^{\bullet -}$ orientation from 285 GHz-EPR data



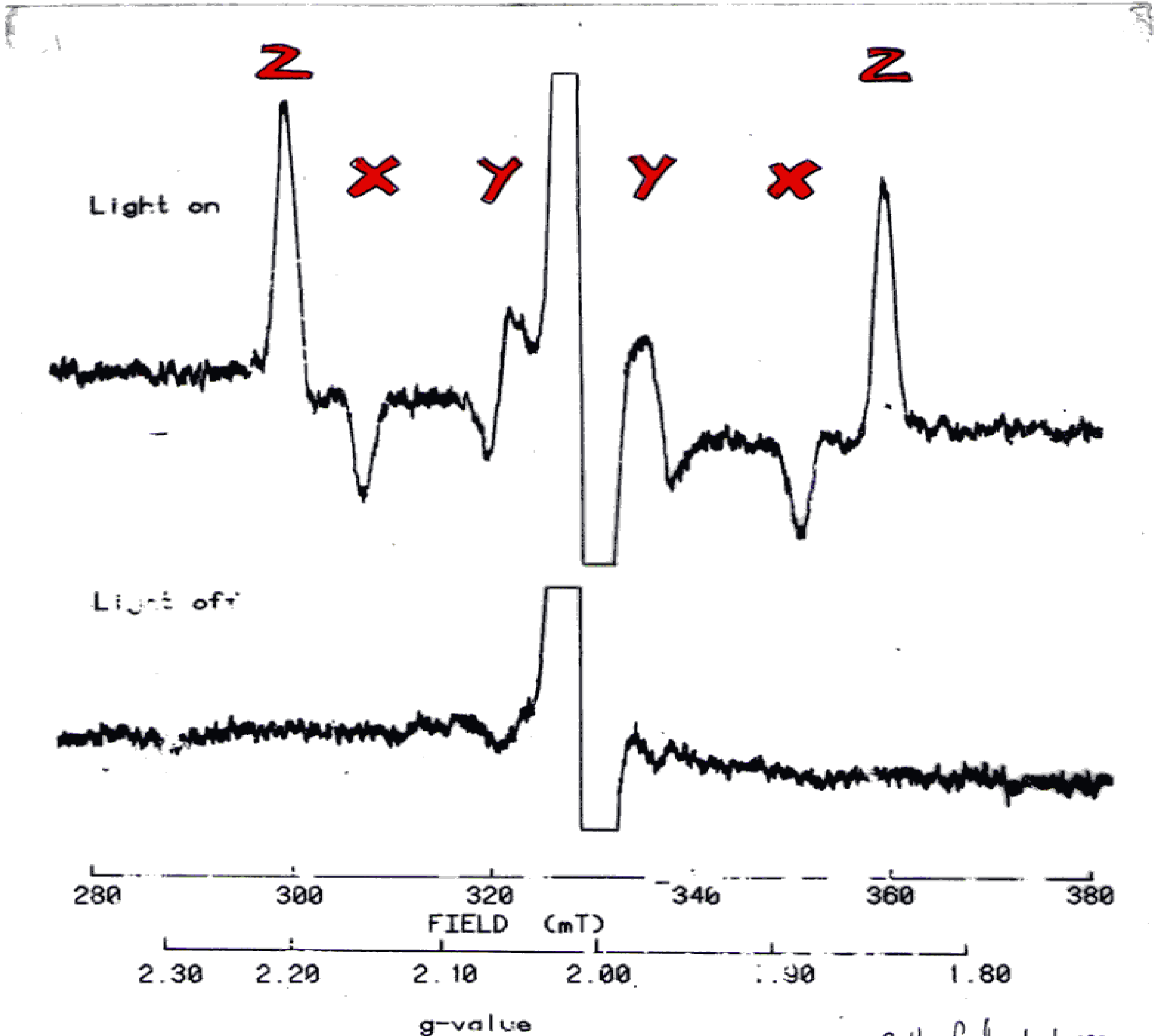
$Tyr_D^{\bullet}$ from 285 GHz-EPR data





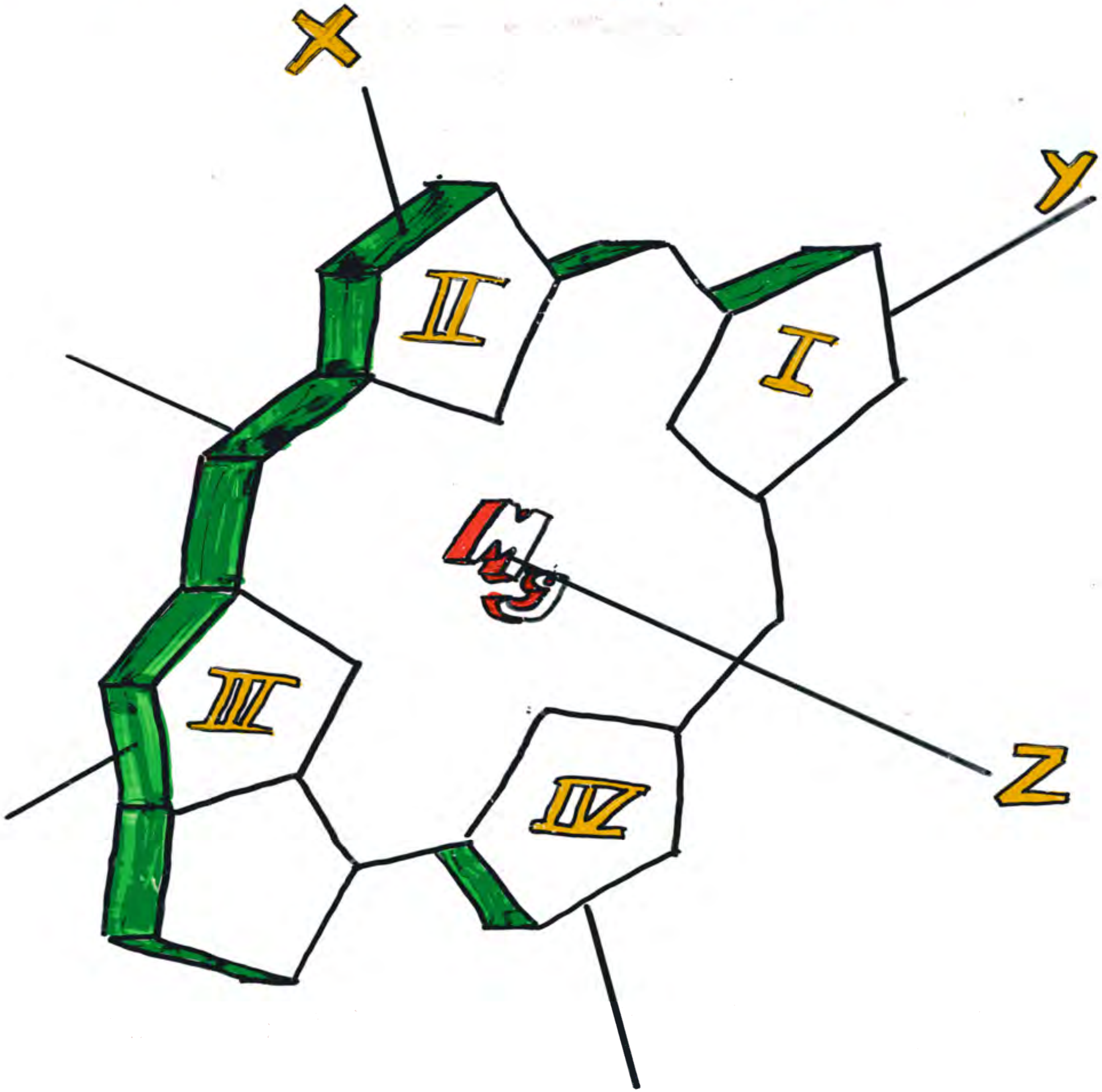
Dorlet et al.
Biochemistry 2000

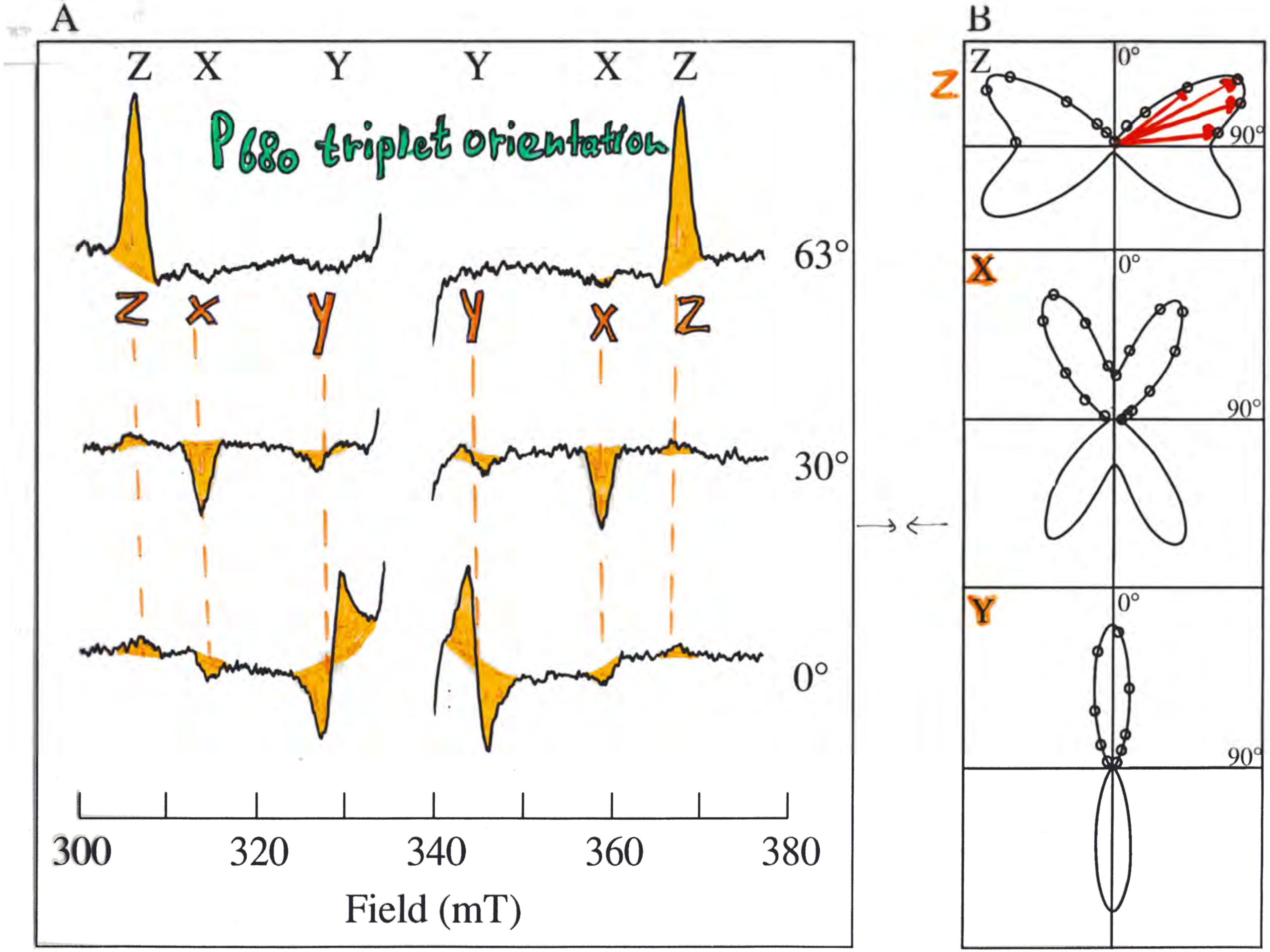
Reaction Centre triplet in PSII



Rutherford et al 1981

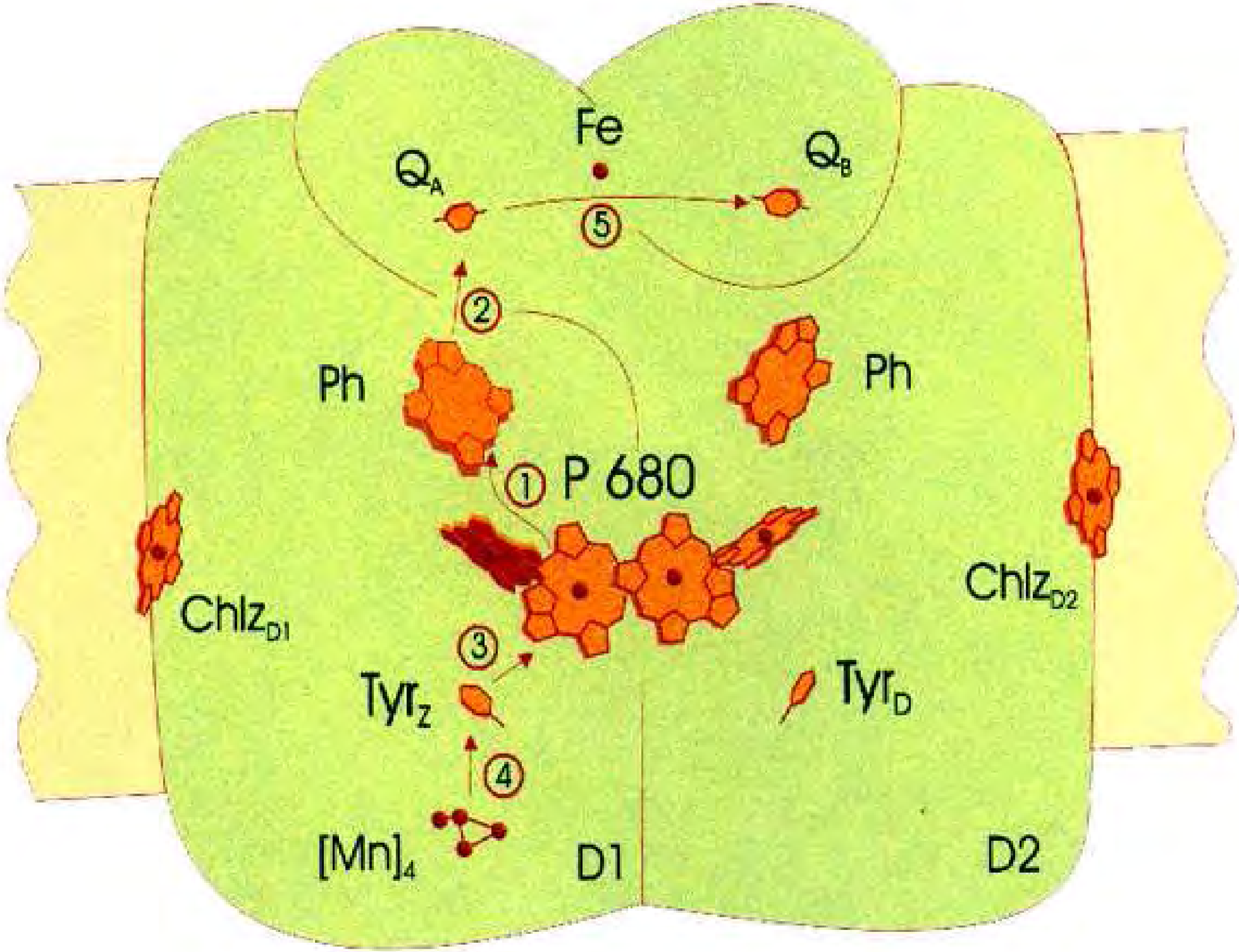
triplet molecular axes of Chl. a in vitro



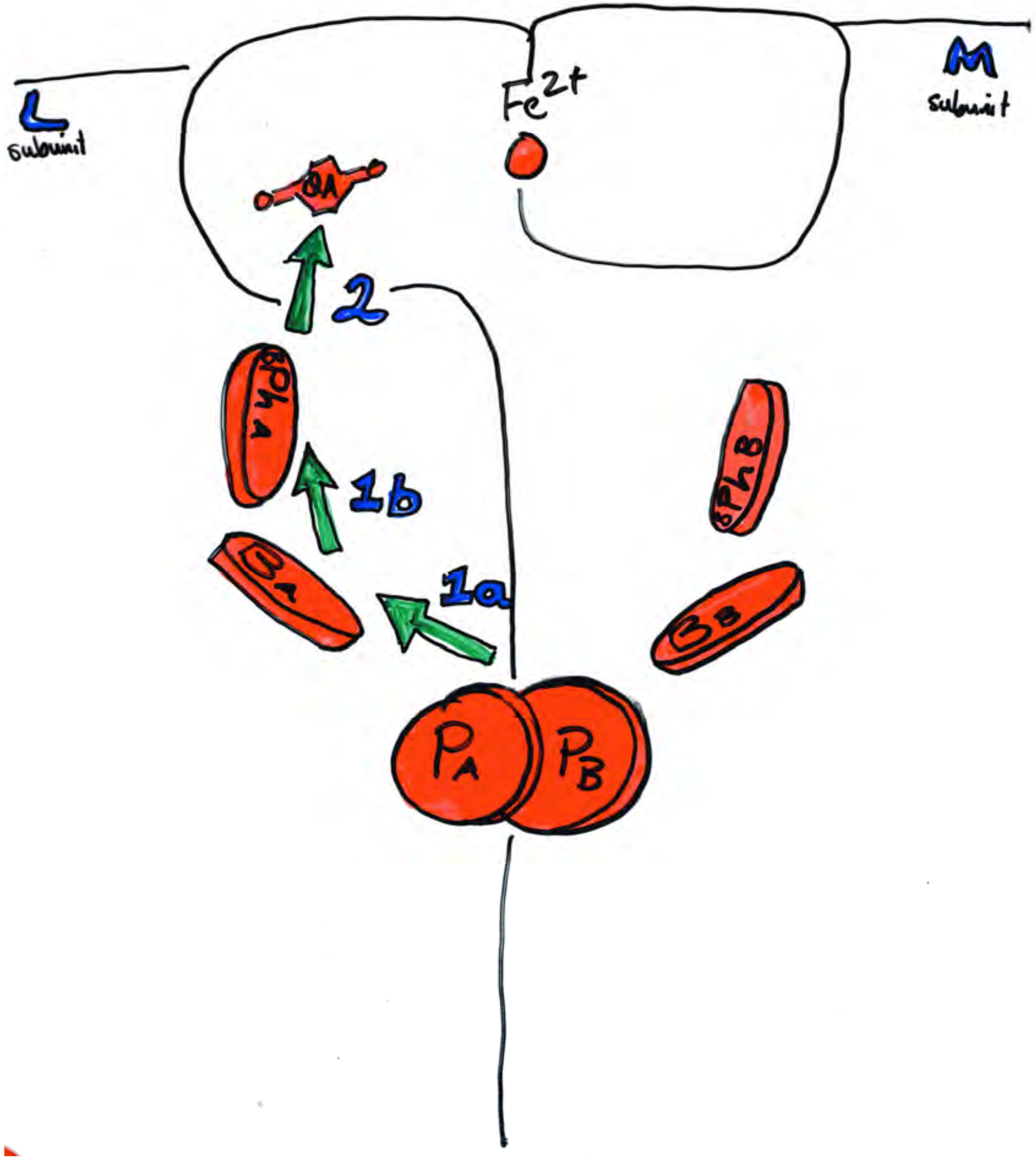


Van Mieghem, Satoh & Rutherford 1991

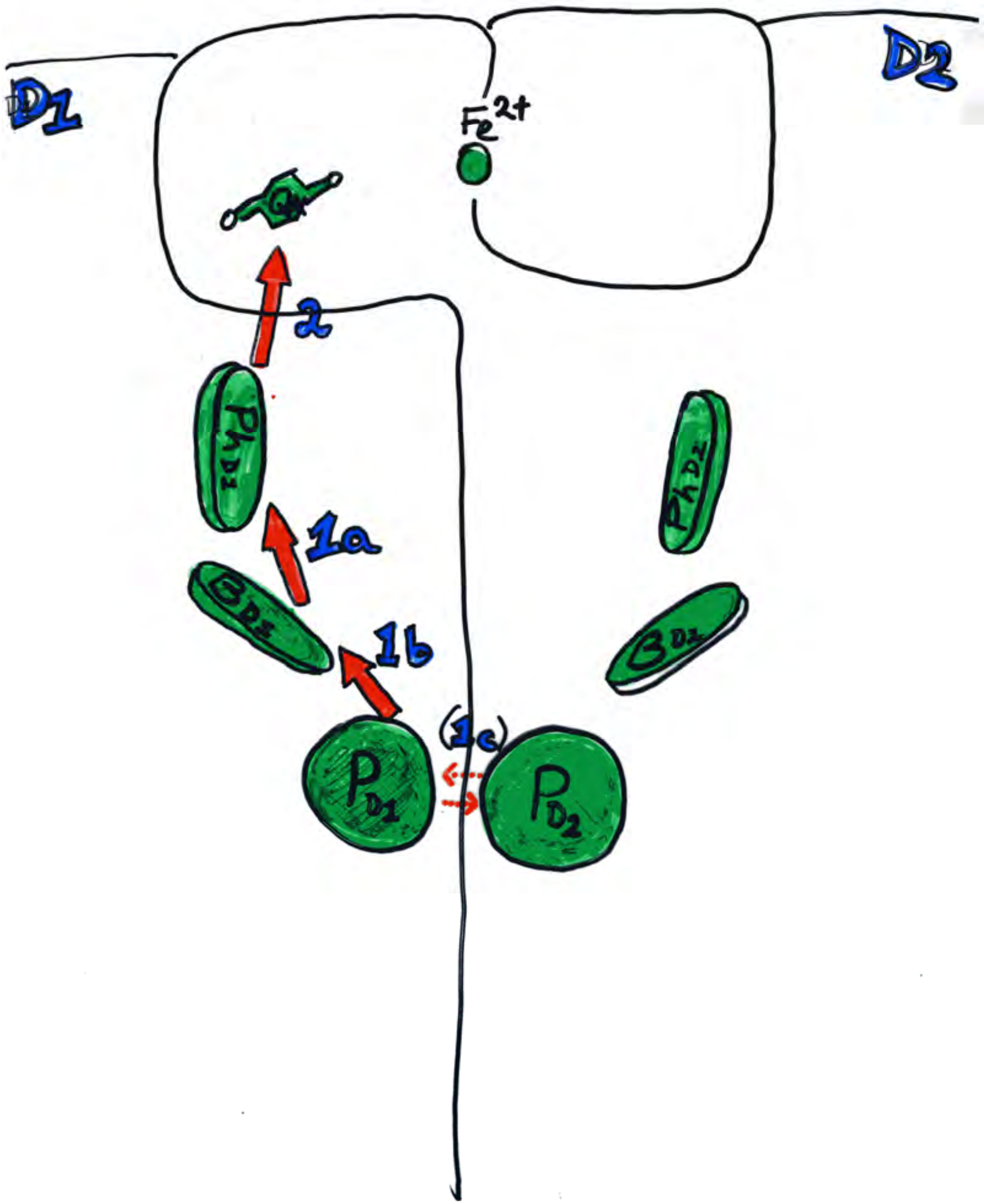
Photosystem II



Charge separation in purple bacterial reaction centres

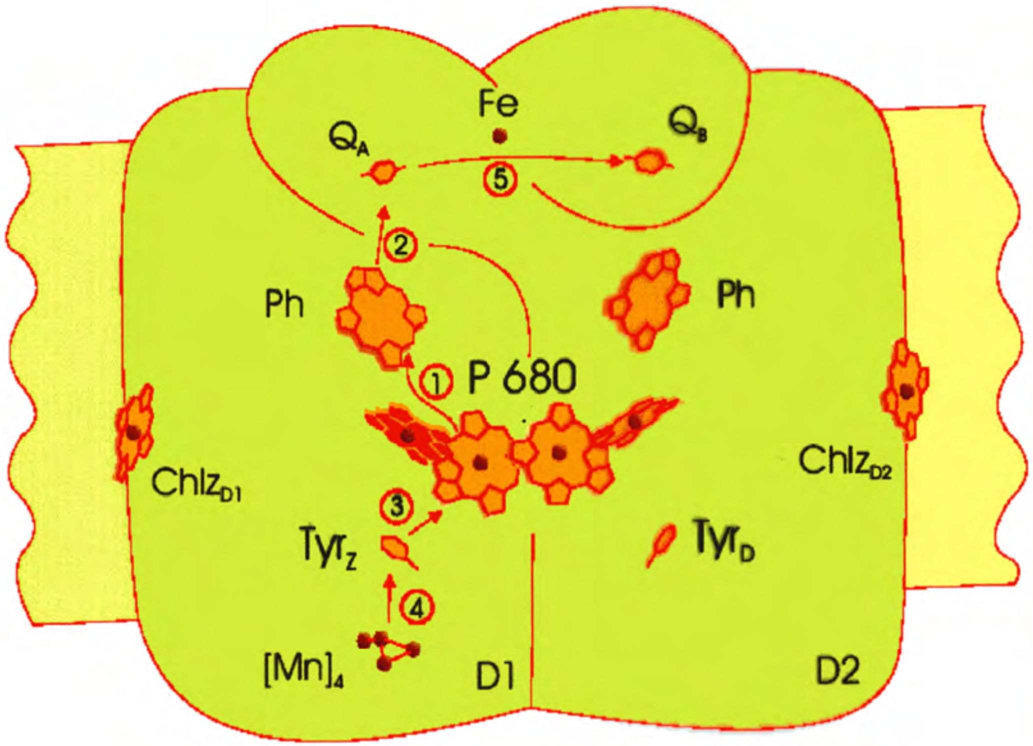


Charge separation in PSII

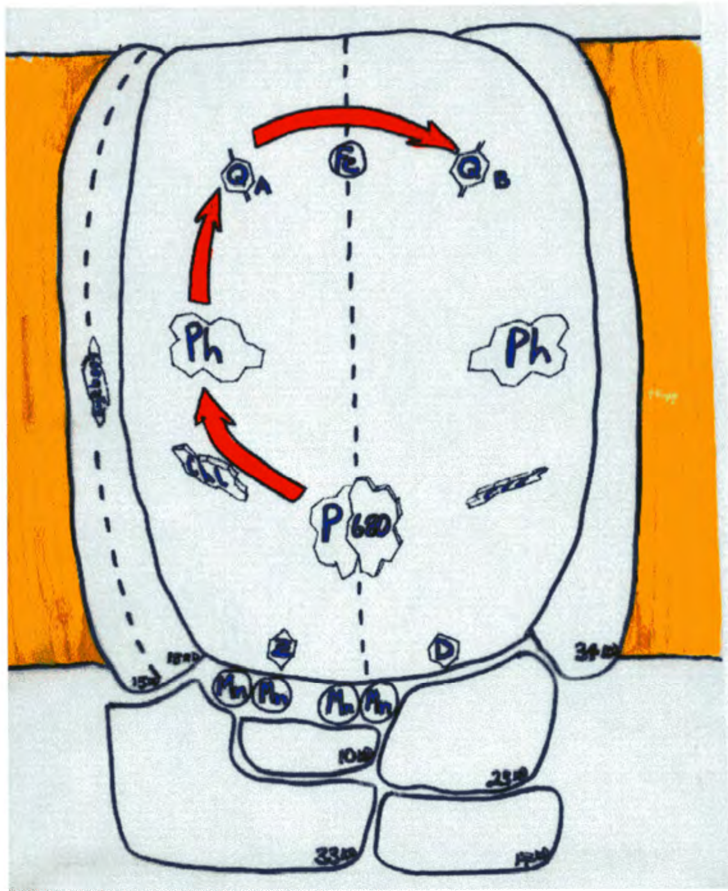


Photosystem II

2003



1985



Phase 4

function and mechanism

herbicides

$Q_A^- \rightarrow Q_B$

electron transfer:
gating mechanism

regulation of
electrontransfer

$Q_A^- \rightarrow Q_B$

electron transfer: gating mechanism

herbicides

regulation of electrontransfer

protection against photodamage

proton-coupled electron transfer

$Q_A^- \rightarrow Q_B$ electron transfer: gating mechanism

herbicides

regulation of electron transfer

protection against photodamage

proton-coupled electron transfer

side pathway donors

$Q_A^- \to Q_B$ electron transfer: gating mechanism

herbicides

regulation of electron transfer

Protection against photodamage

proton-coupled electron transfer

side pathway donors

$Q_A^- \rightarrow Q_B$ electron transfer: gating mechanism

photoassembly of the Mn cluster

herbicides

regulation of electron transfer

protection against photodamage

WATER OXIDATION

proton-coupled electron transfer

Side pathway donors

$Q_A^- \to Q_B$ electron transfer: gating mechanism

photoassembly of the Mn cluster

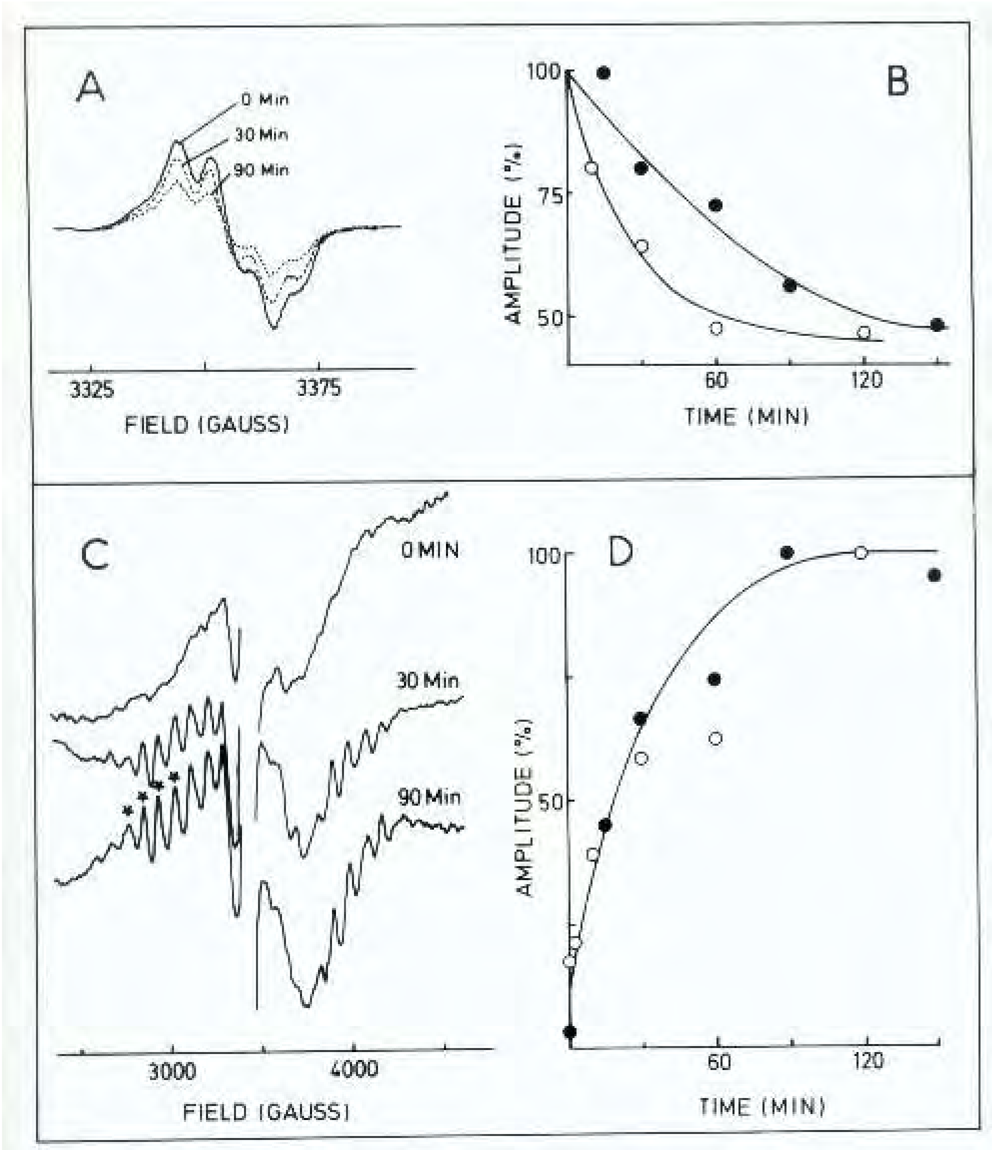
herbicides

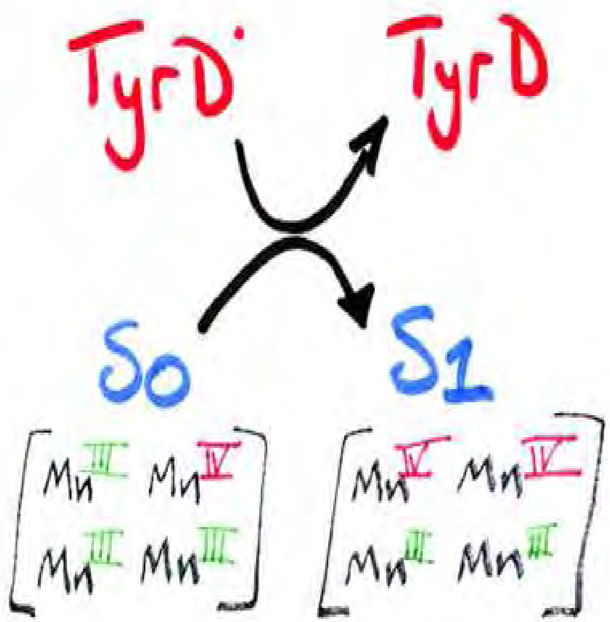
regulation of electron transfer

Protection against photodamage

TyrD• can oxidize the Mn_4 : $S_0 \rightarrow S_1$

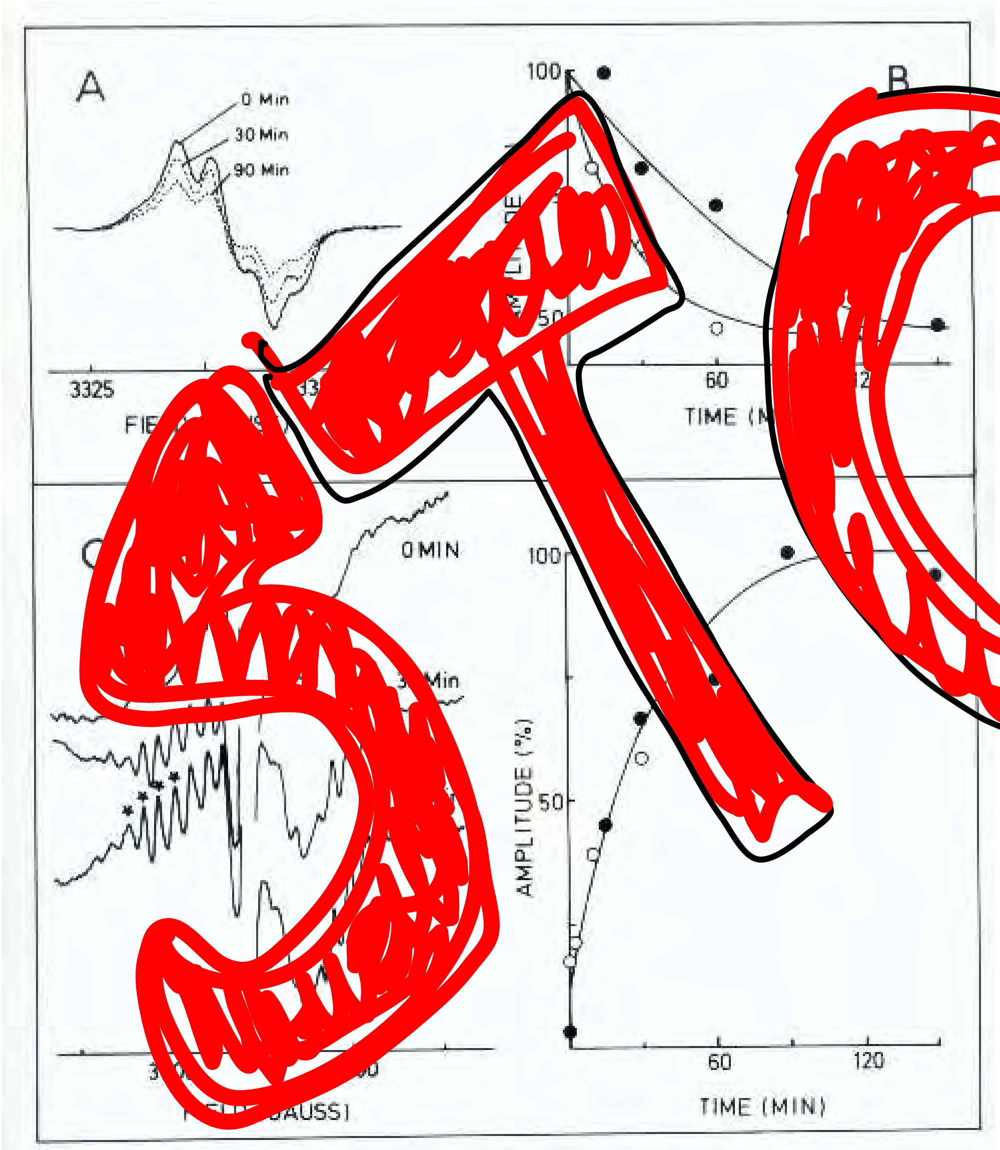
Styring & Rutherford 87

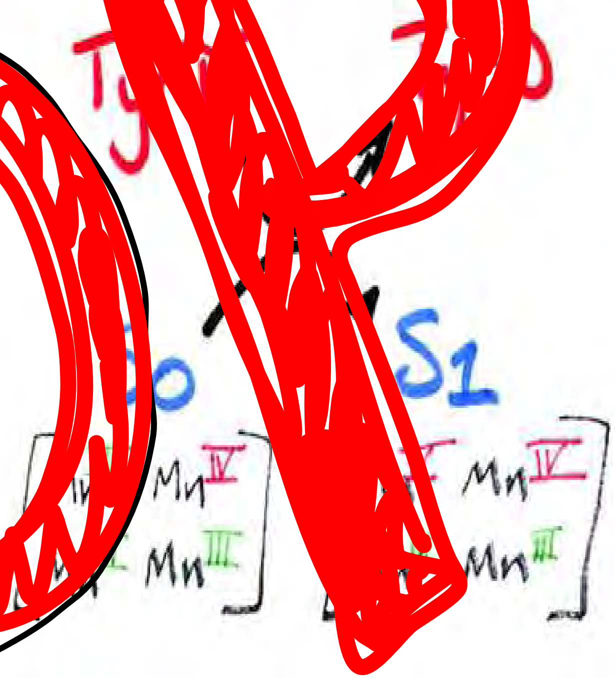




a role in photoactivation

TyrD• can oxidize the Mn_4 : $S_0 \rightarrow S_1$

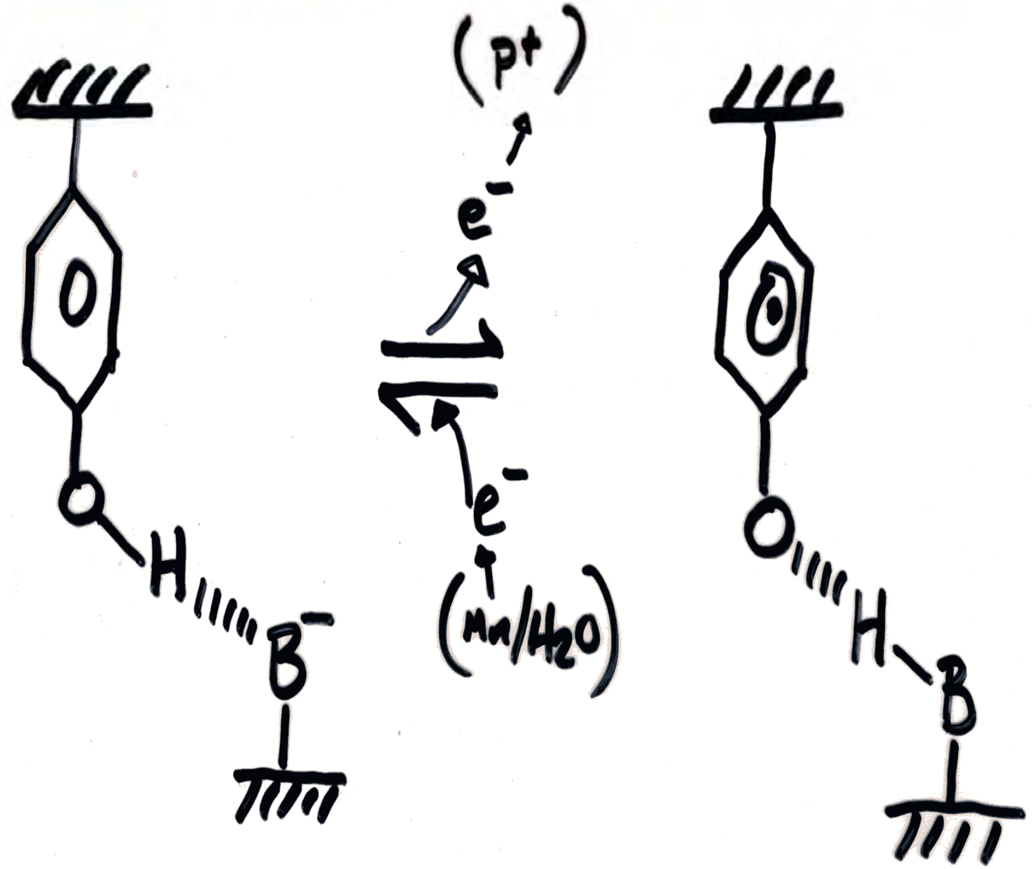




a role in photoactivation

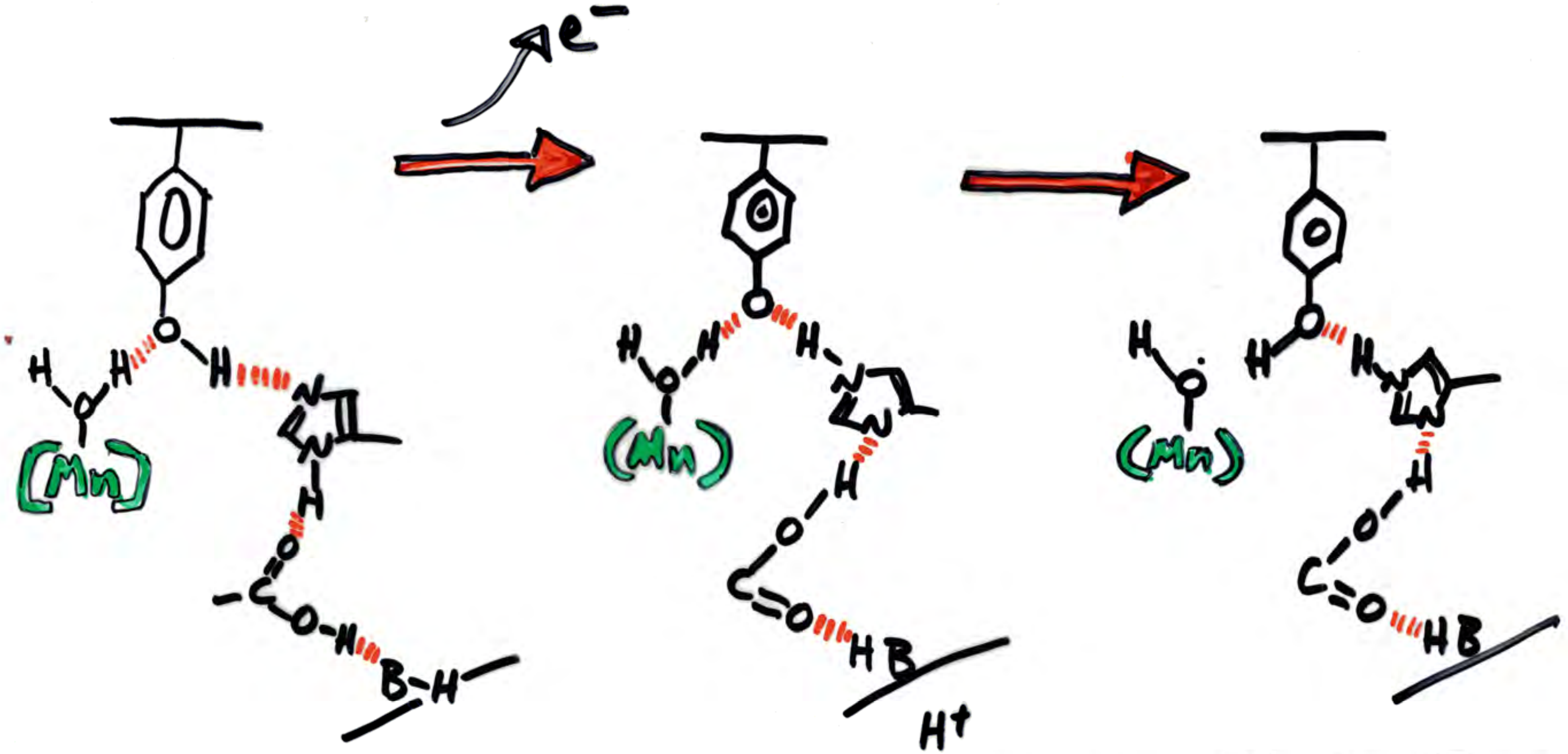
Role of Tyrosyl radical

1 Electron transfer intermediate



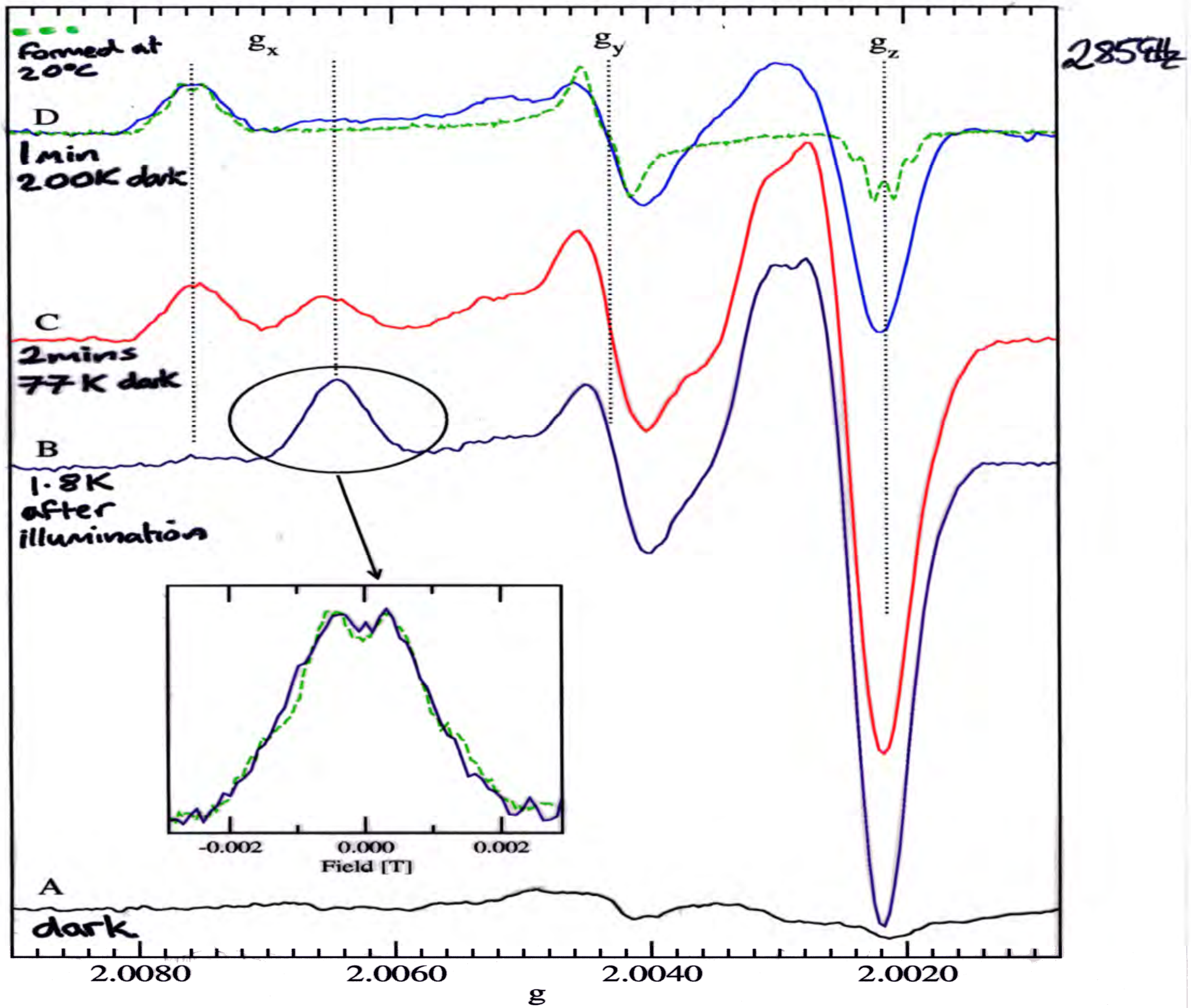
Role of Tyrosyl radical

2 Abstractor of both an electron and a proton (H atom?) from H_2O (Mn)



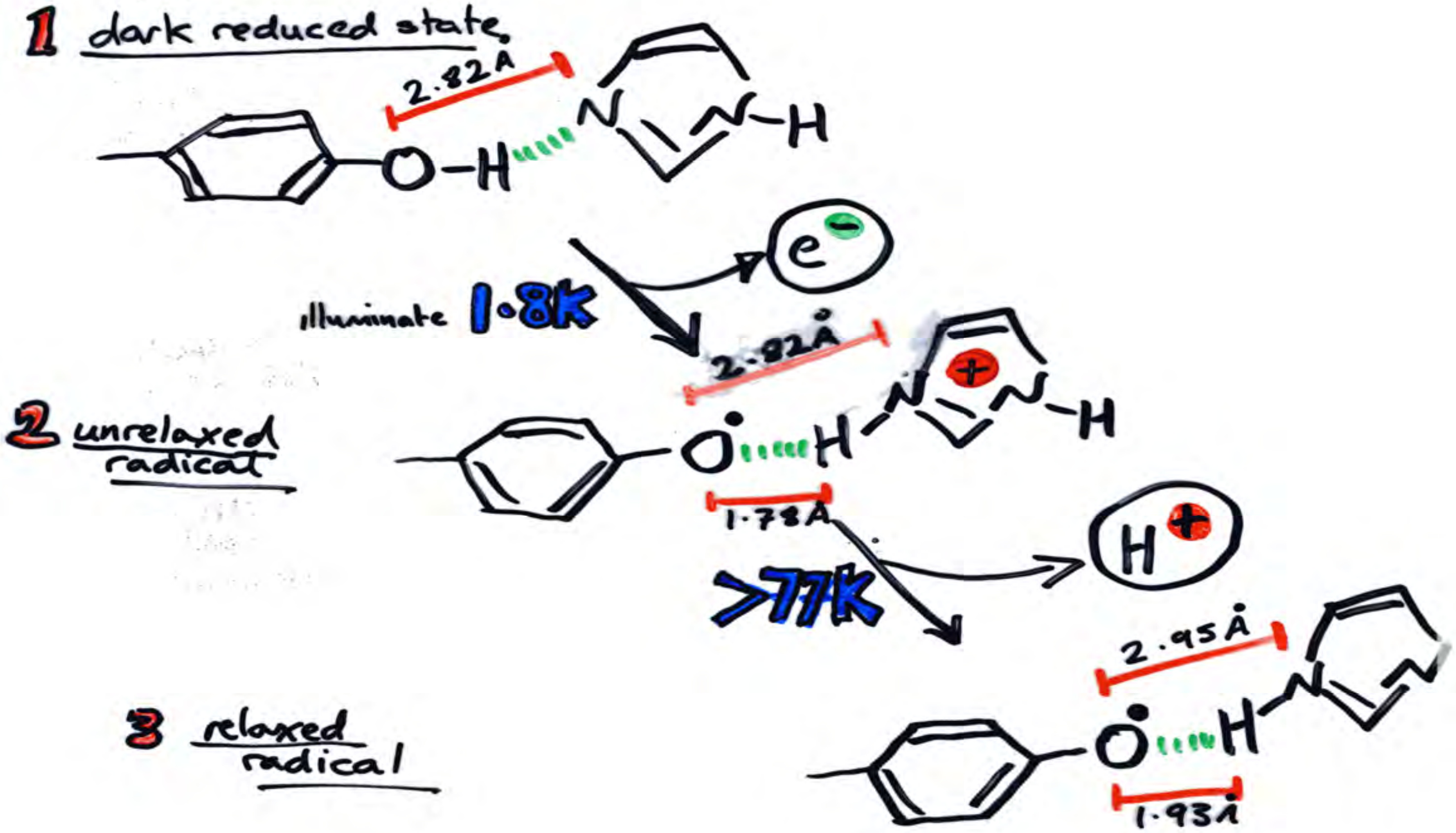
based on Babcock & Tommos

Tyr D oxidation at cryogenic temperature



Faller et al 2003

Model a : protontunnelling (pcet)



the sequential electrostatic environments track proton movements (or compensation) why are we interested?

Why are we interested?

1. fundental interests
   - the enzyme that changed the world!

2. applied interests
   - Agriculture
   - Ecology
   - Energy

herbicides

growth/yields

photoinhibition

atmosphere

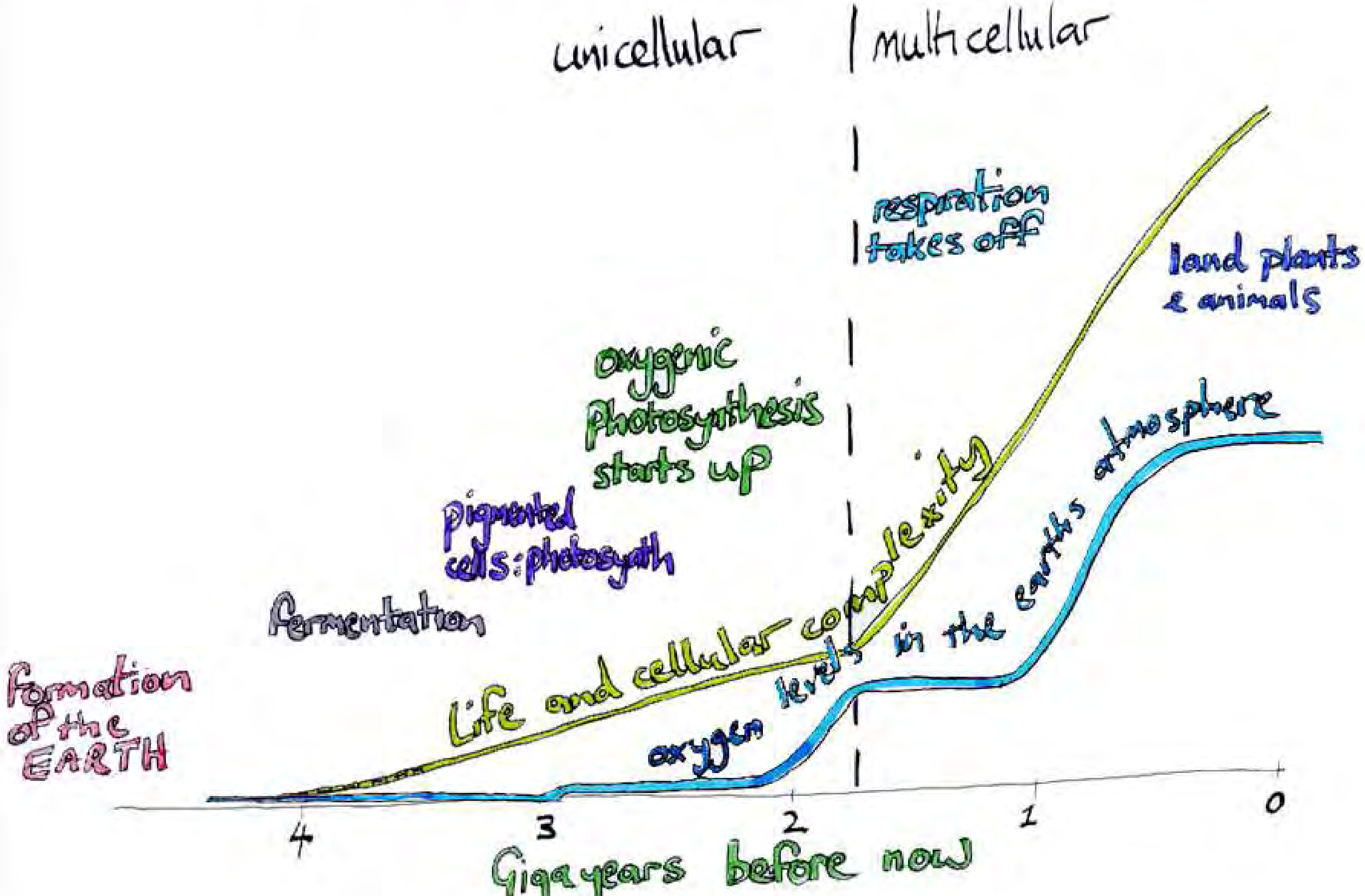
biomass

petrochemicals

biohydrogen

biomimetic chemistry

LIFE ON EARTH: an overview



Photosynthesis

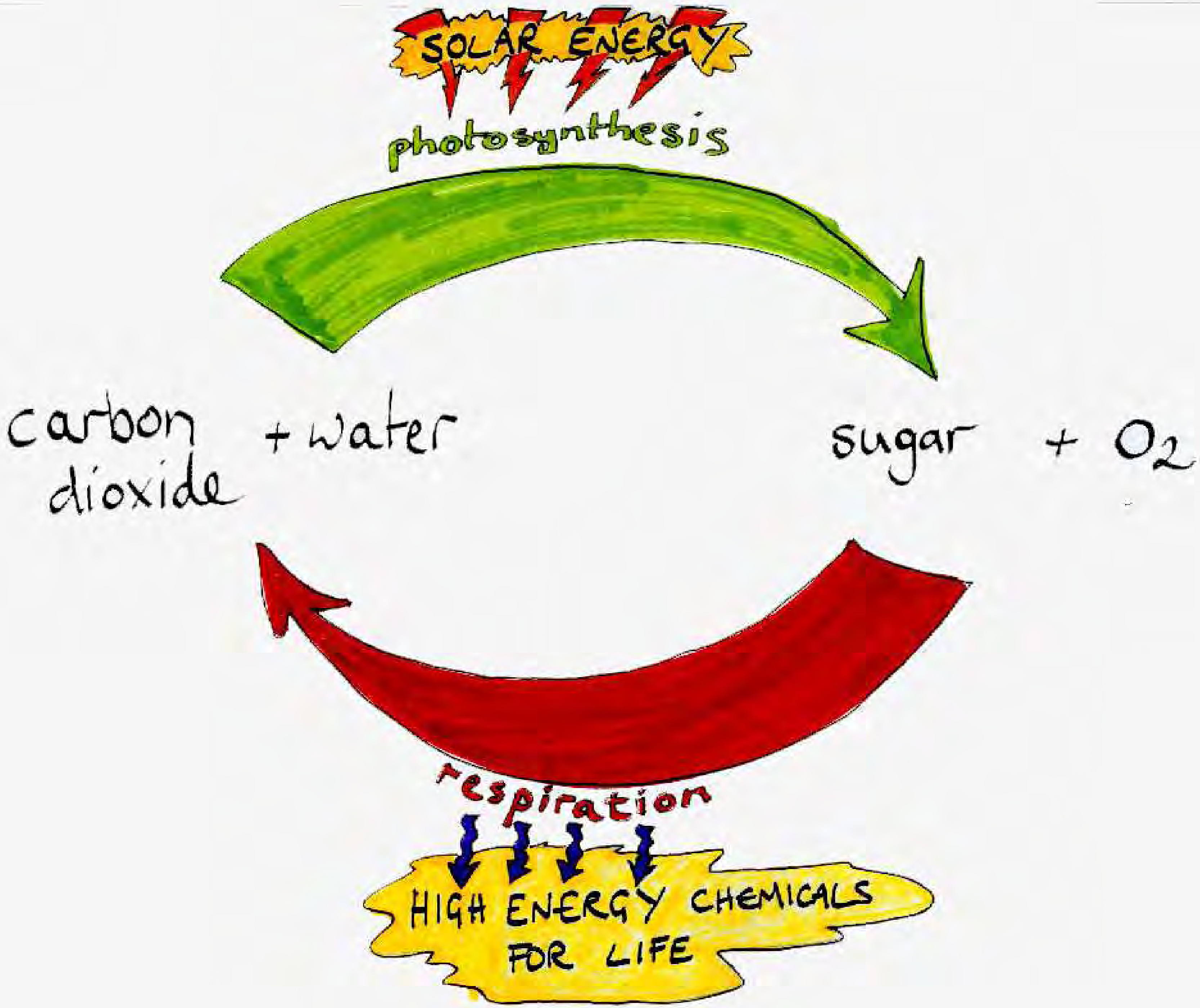
Water + Carbon dioxide ⟶ Sugar + Oxygen

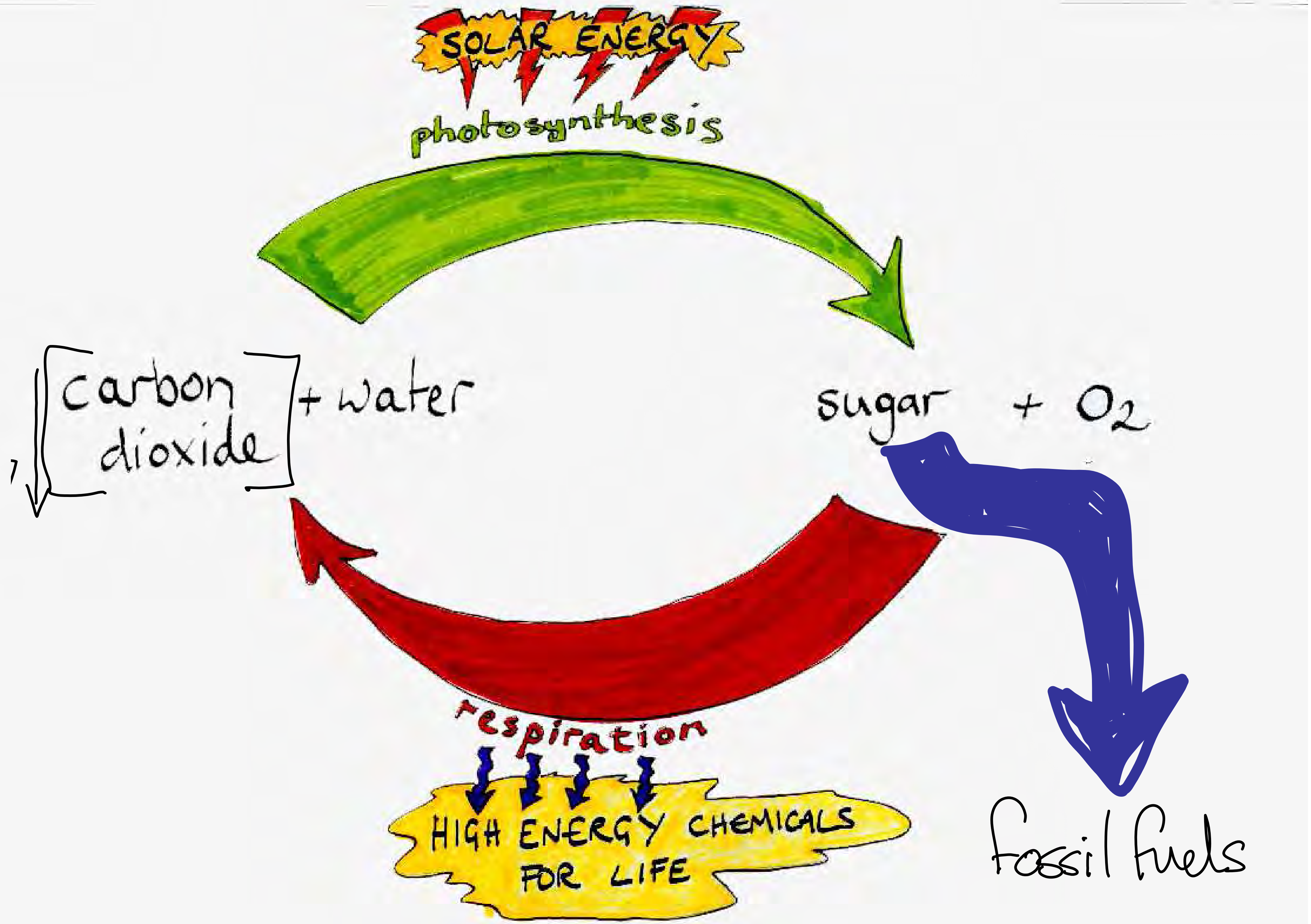
energy input for the living world

Respiration

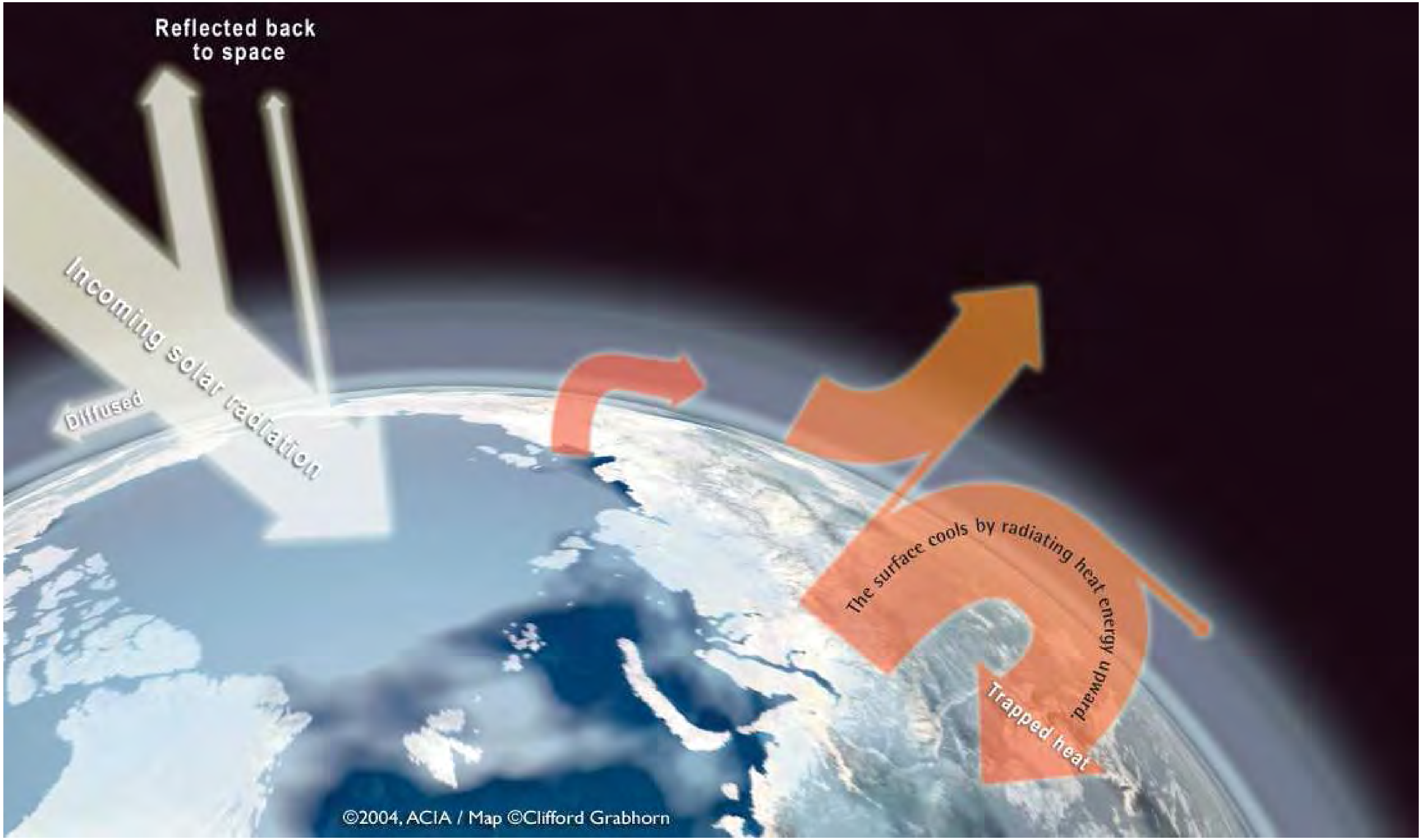
Oxygen + Sugar → Water + Carbon dioxide

↳ ENERGY


SOLAR ENERGY
photosynthesis
carbon dioxide
+ water
sugar
+ O2
respiration
HIGH ENERGY CHEMICALS FOR LIFE


SOLAR ENERGY
photosynthesis
carbon dioxide
+ water
sugar
+ O_2
respiration
HIGH ENERGY CHEMICALS FOR LIFE
fossil fuels

CO2 → the greenhouse effect → global warming



Roles for photosynthesis research on the energy issue?

1 Plant growth agriculture, biomass, environmental stress biofuels, etc

2 Microbial growth biomass, biohydrogen, biofuels, stress

3 Artificial photosynthesis catalysts, biomimetics

SOLAR ENERGY

Roles for photosynthesis research on the energy issue?

1 Plant growth — agriculture, biomass, environmental stress, biofuels, etc

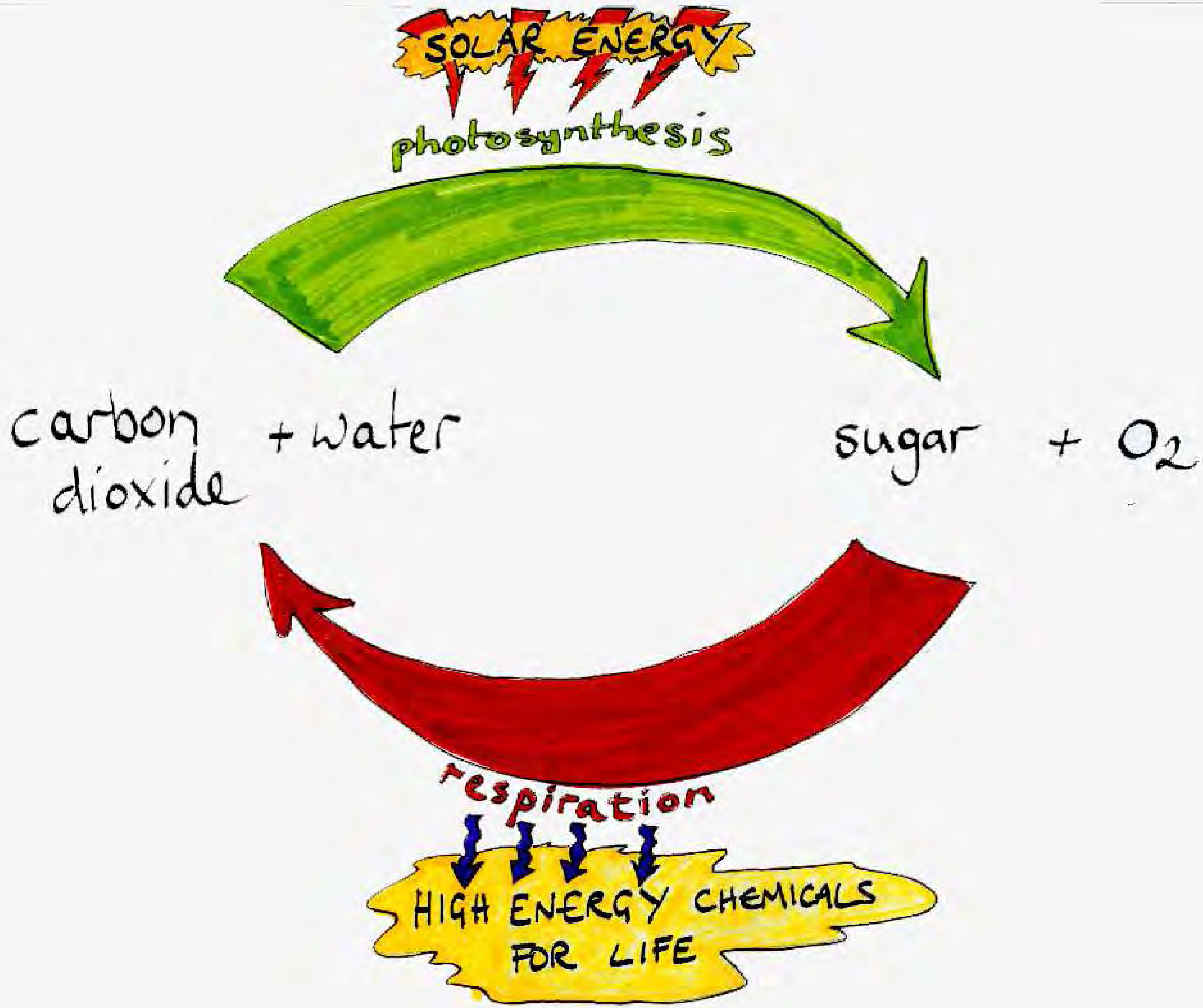
2 Microbial growth — biomass, biohydrogen, biofuels, stress

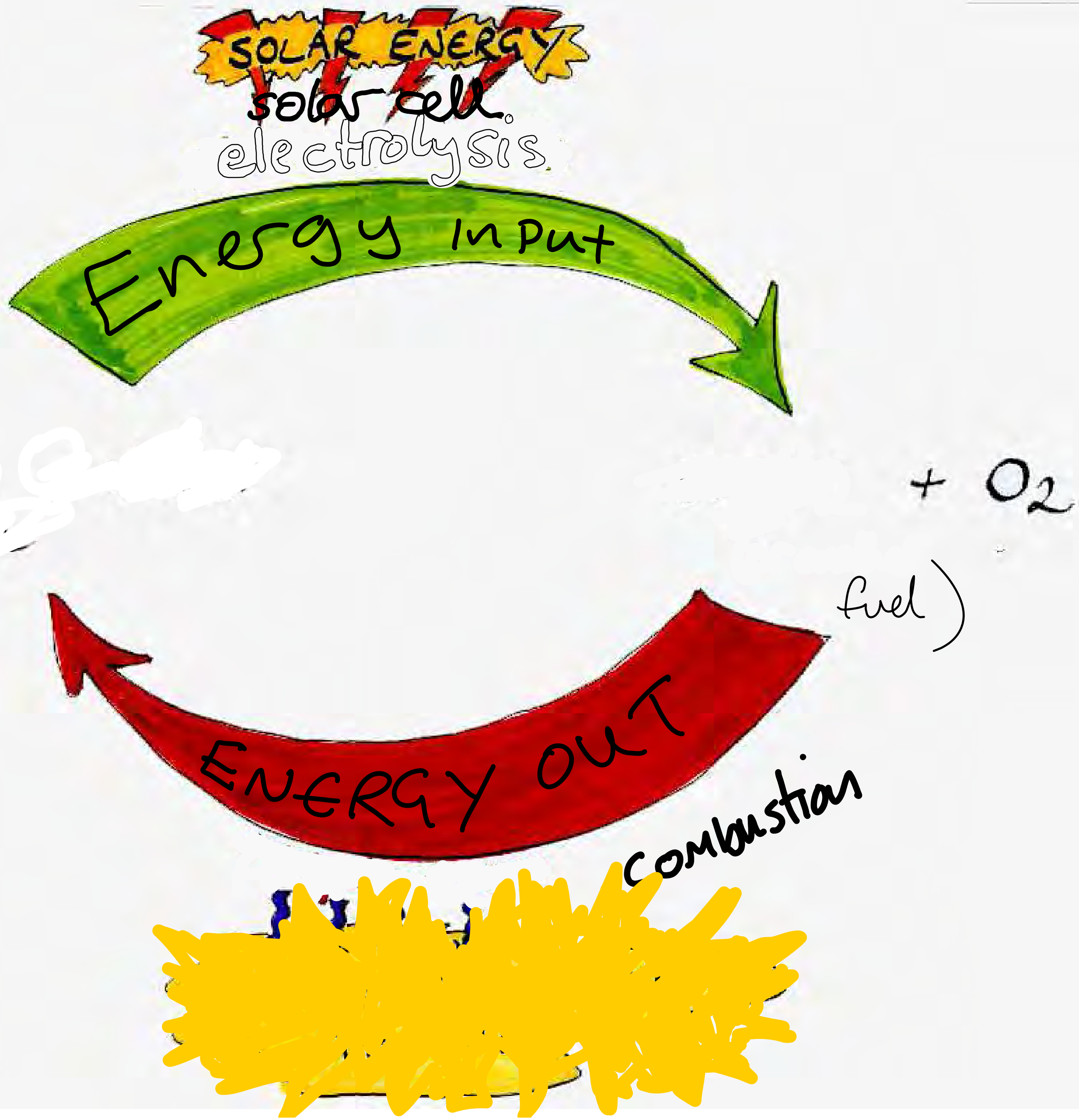
3 Artificial photosynthesis — catalysts, biomimetics

SOLAR ENERGY

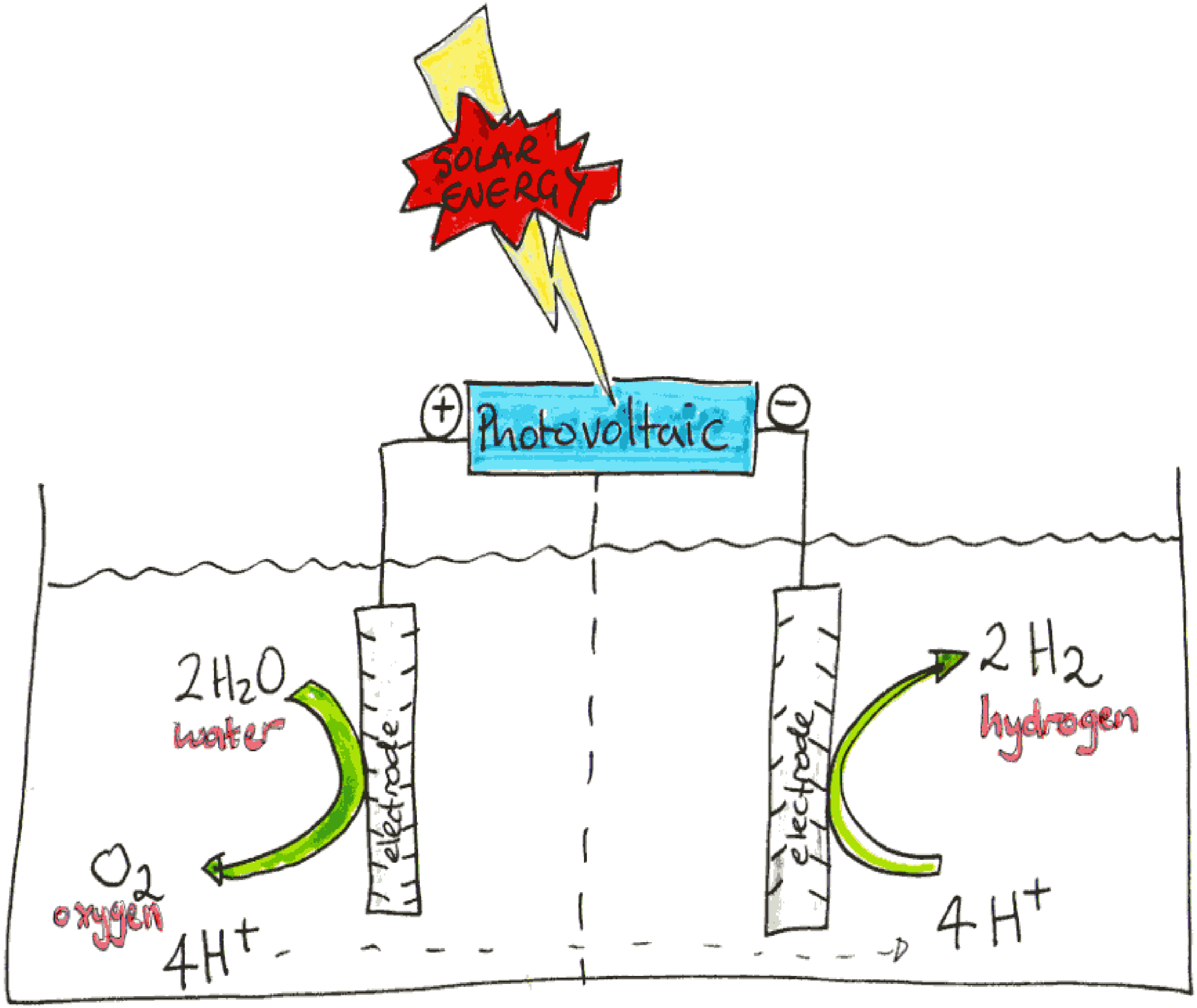
the solution ?

photovoltaics


SOLAR ENERGY
photosynthesis
carbon dioxide + water
sugar + O2
respiration
HIGH ENERGY CHEMICALS FOR LIFE


SOLAR ENERGY
solar cell
electrolysis
Energy input
+ O_2
fuel)
ENERGY OUT
combustion

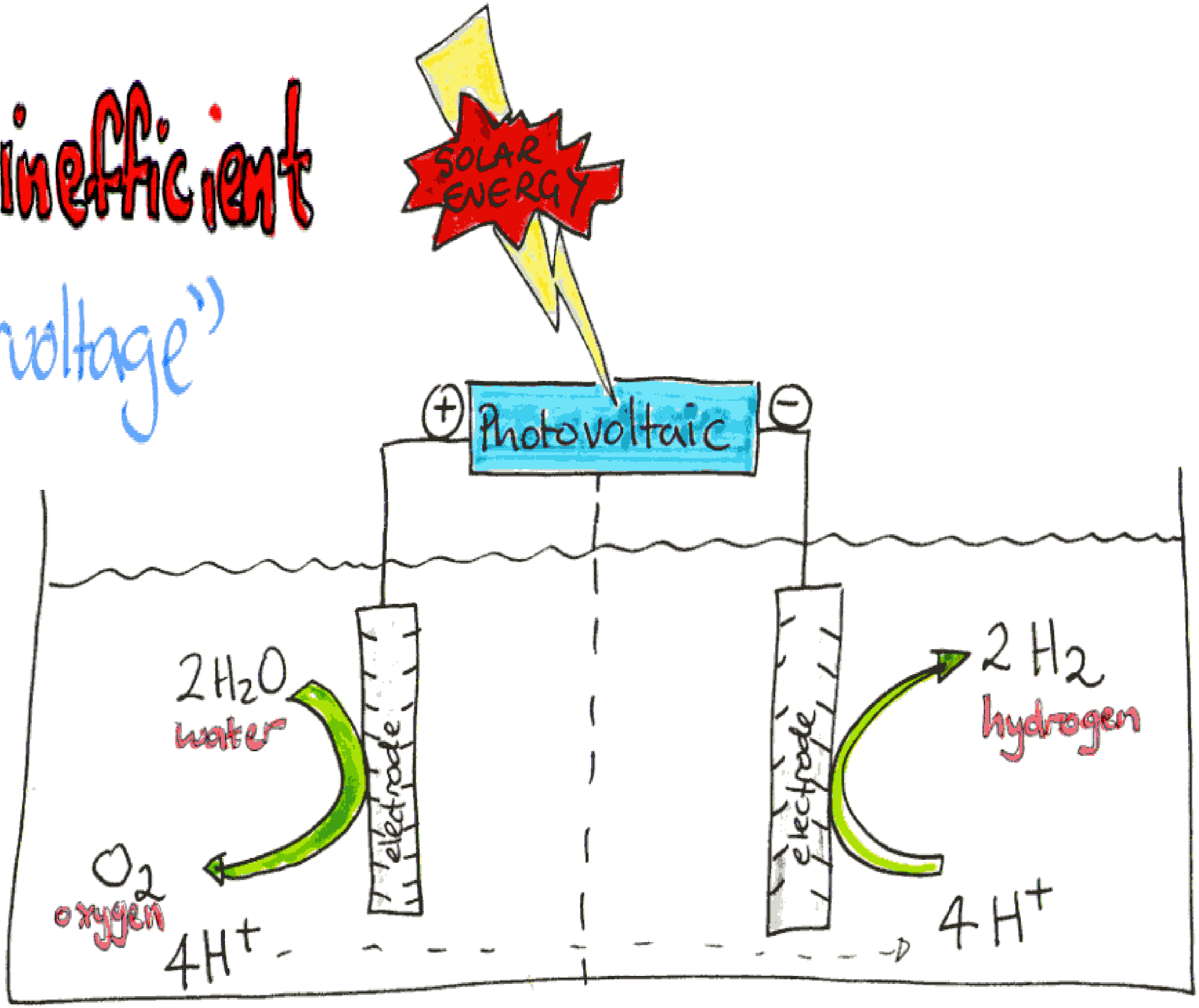
Photovoltaic driven electrolysis



Photovoltaic driven electrolysis

but inefficient

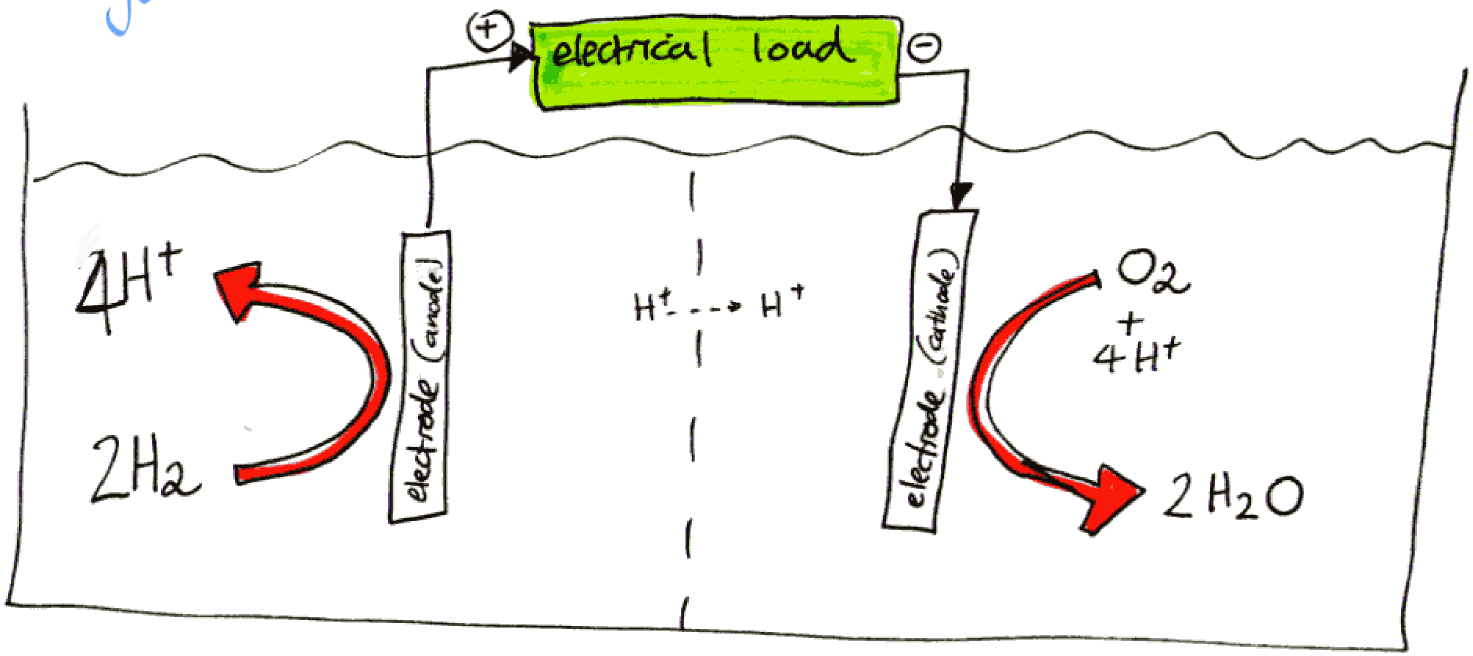
"big "overvoltage""



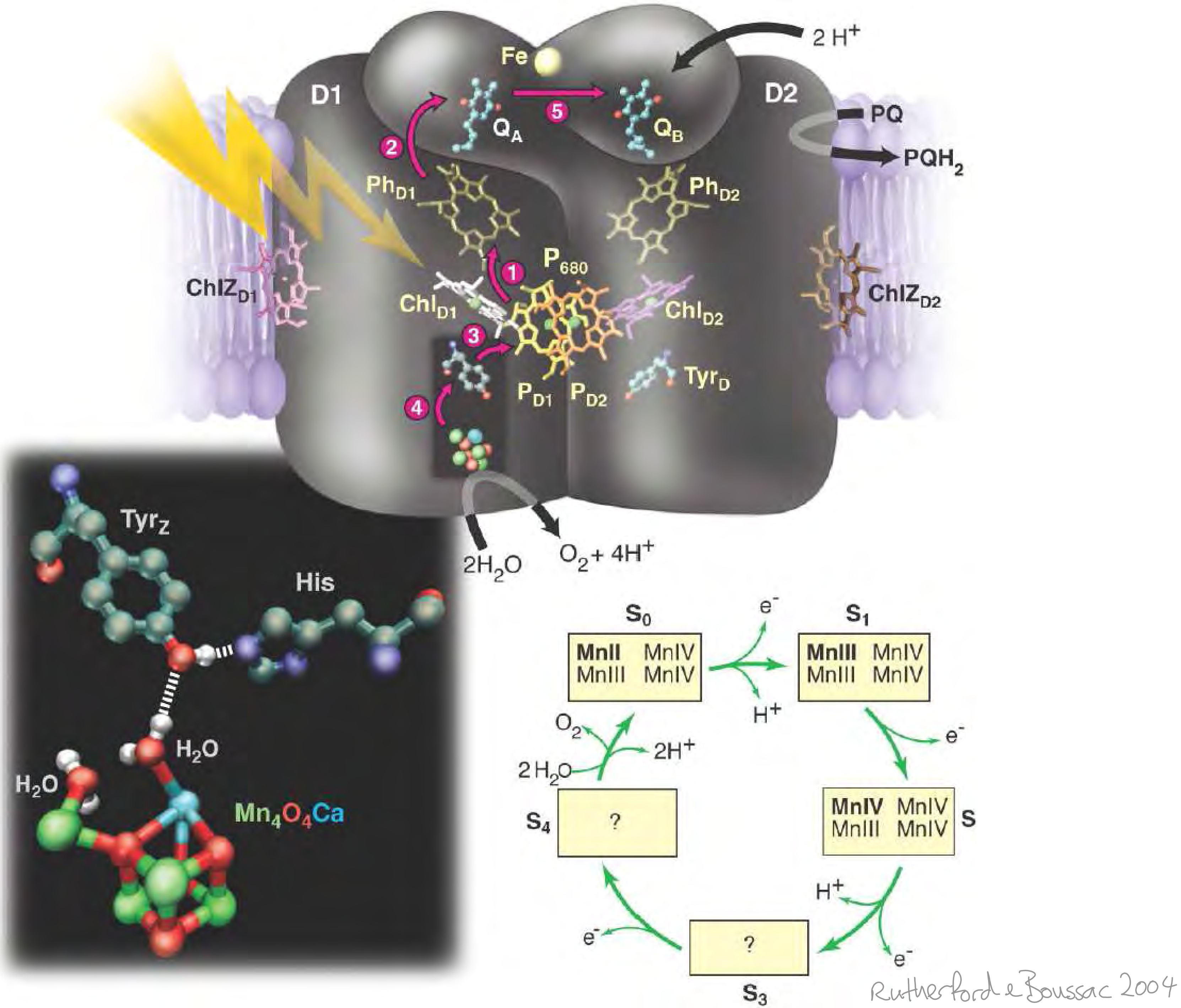
A hydrogen fuel cell

but inefficient

big "overvoltage"



there is only one catalyst known that is capable of oxidizing water with a low over-potential.....



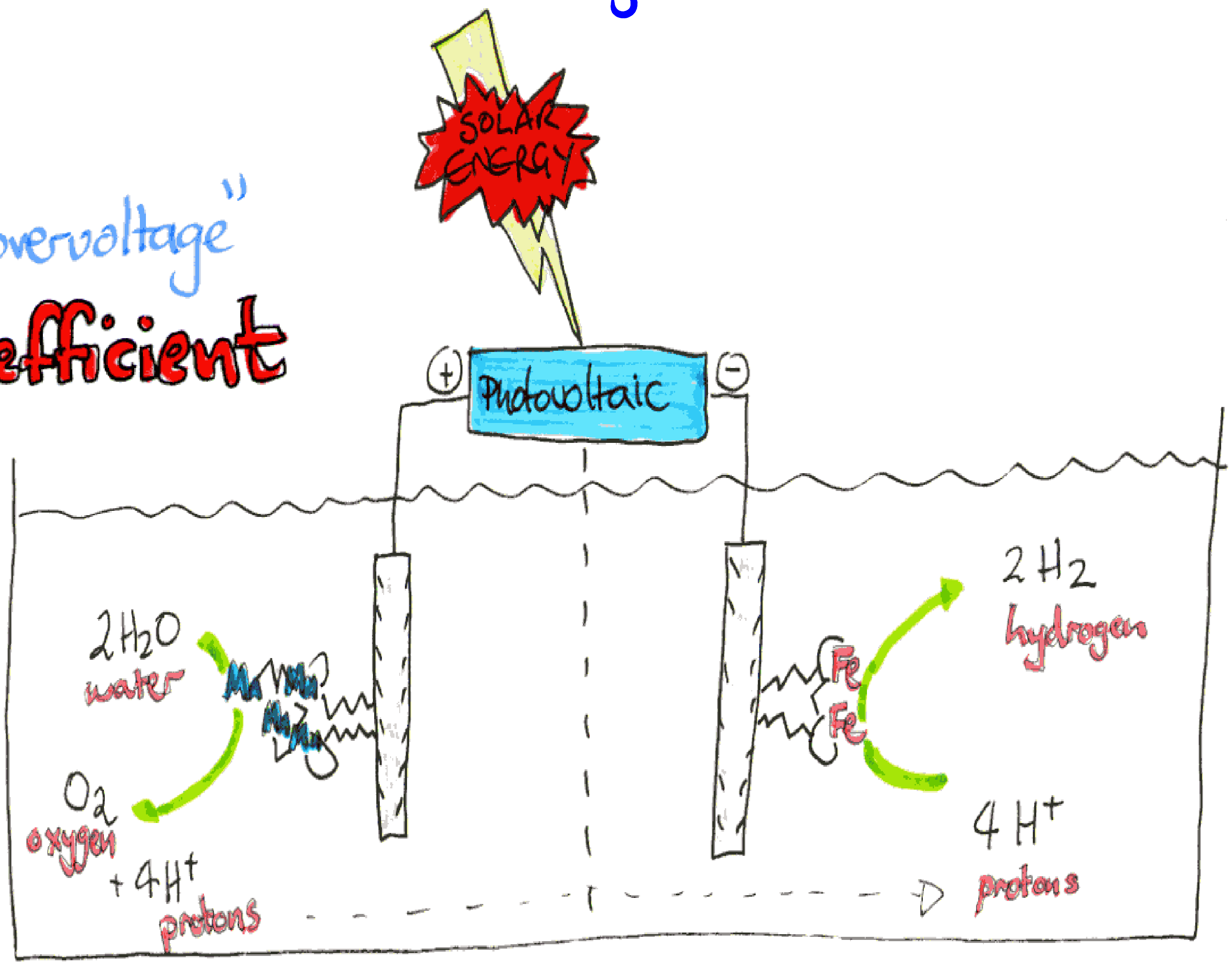
2 H+
Fe
D1
D2
PQ
PQH2
QA
QB
PhD1
PhD2
P680
ChlZD1
ChlZD2
ChlD1
ChlD2
TyrD
PD1
PD2
2H2O
O2 + 4H+
TyrZ
His
H2O
H2O
Mn4O4Ca
S0
S1
MnII MnIV
MnIII MnIV
MnIII MnIV
MnIII MnIV
MnIV MnIV
MnIII MnIV
S
S4
S3
?
?
e-
H+
O2
2H+
2 H2O
Rutherford e Boussac 2004

Can bioinspired catalysts improve efficiencies?

a) the electrolysis cell

small "overvoltage"

more efficient

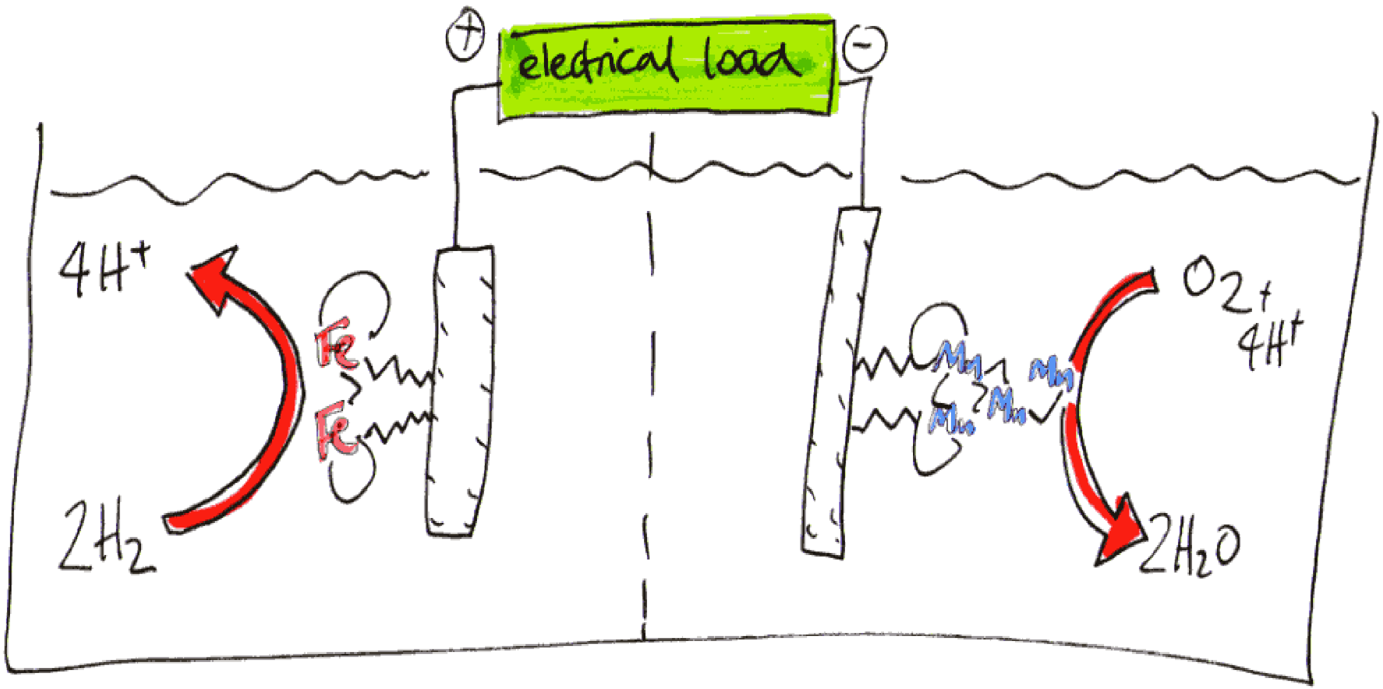


Can bioinspired catalysts improve efficiencies?

b) the fuel cell

small "overvoltage"

more efficient



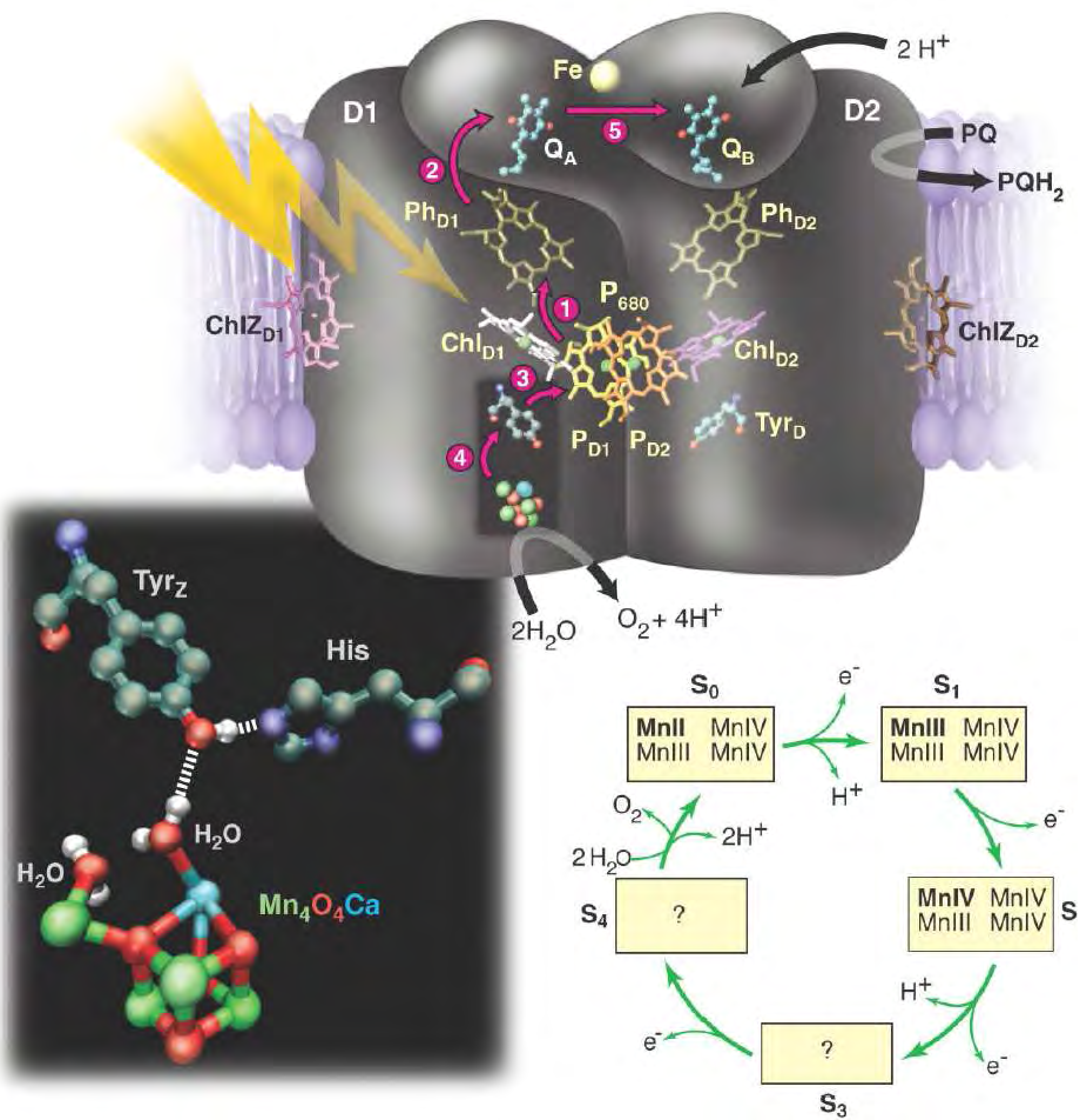
First aim:

to design and make new catalysts inspired by

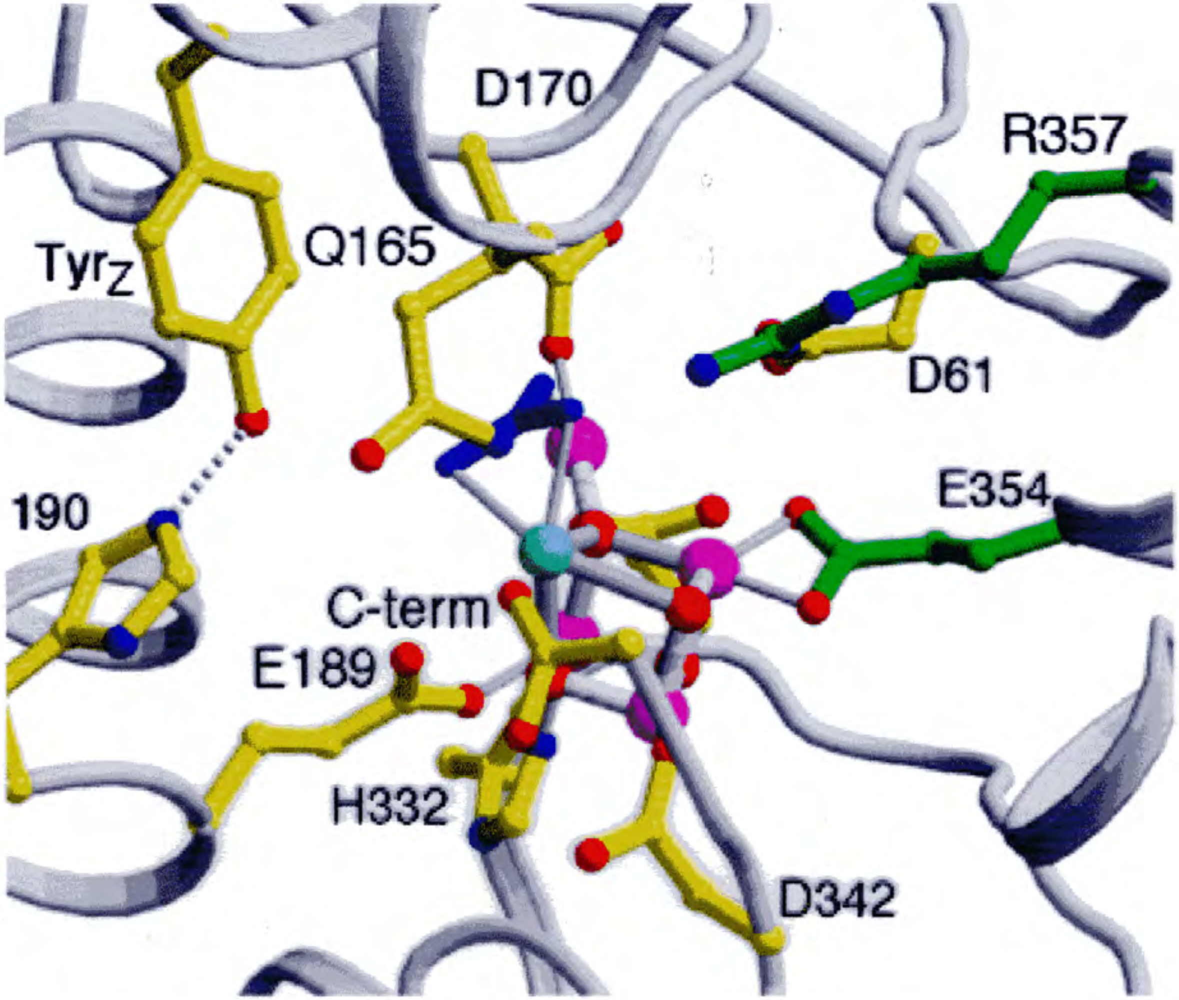
1 the water splitting enzyme

(2 hydrogenases)

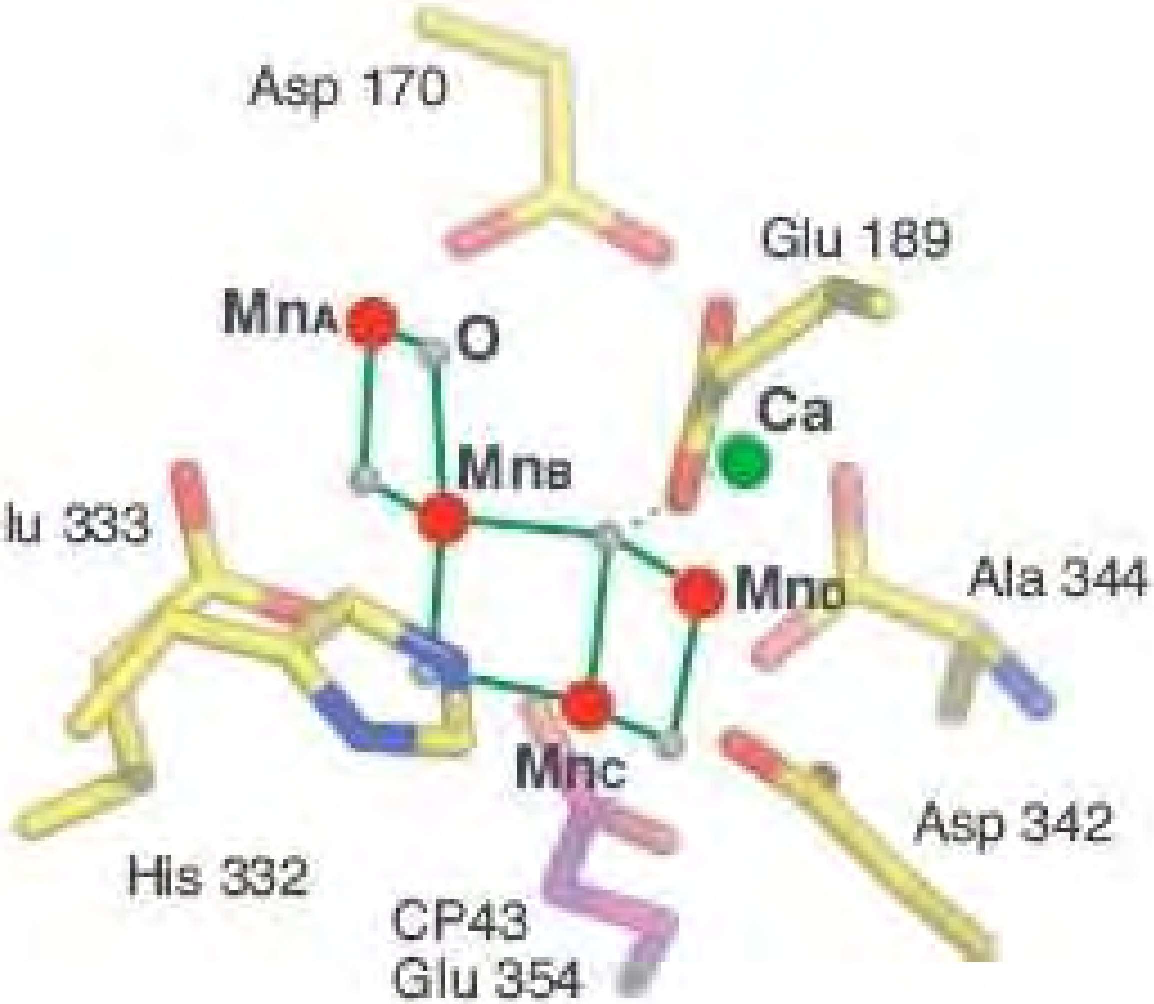
now we have
a target structure



2 H+
Fe
D1
D2
5
QA
QB
PQ
PQH2
2
PhD1
PhD2
1
P680
ChlZD1
ChlD1
ChlD2
ChlZD2
3
TyrD
4
PD1
PD2
2H2O
O2+ 4H+
TyrZ
His
H2O
H2O
Mn4O4Ca
S0
MnII MnIV
MnIII MnIV
e-
H+
S1
MnIII MnIV
MnIII MnIV
e-
O2
2H+
2 H2O
S4
?
MnIV MnIV
MnIII MnIV
S
H+
e-
?
e-
S3



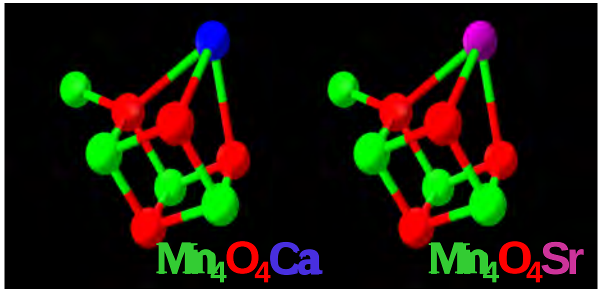
Ferreira et al 2004

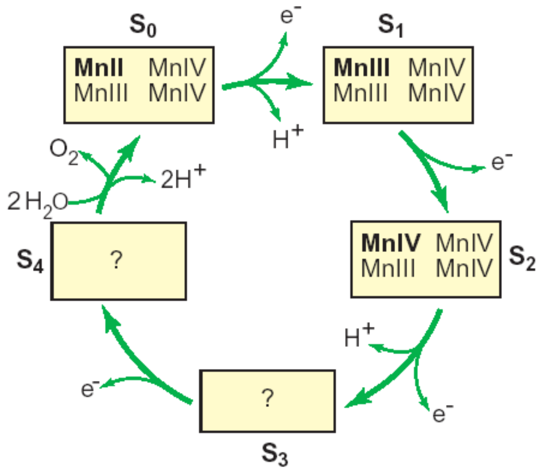


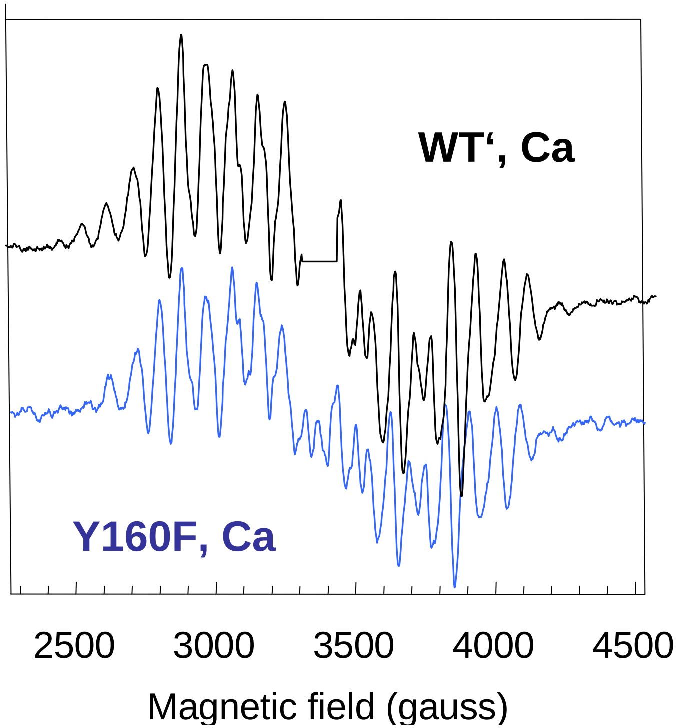
Yano et al 2007

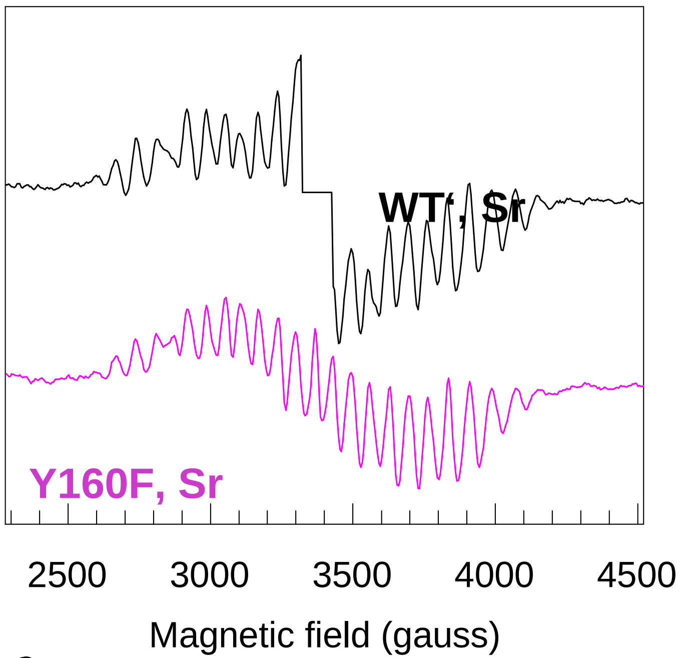
okay, it's still
a bit fuzzy
but it's getting there

Biosynthetic replacement of Ca^{2+} with Sr^{2+}



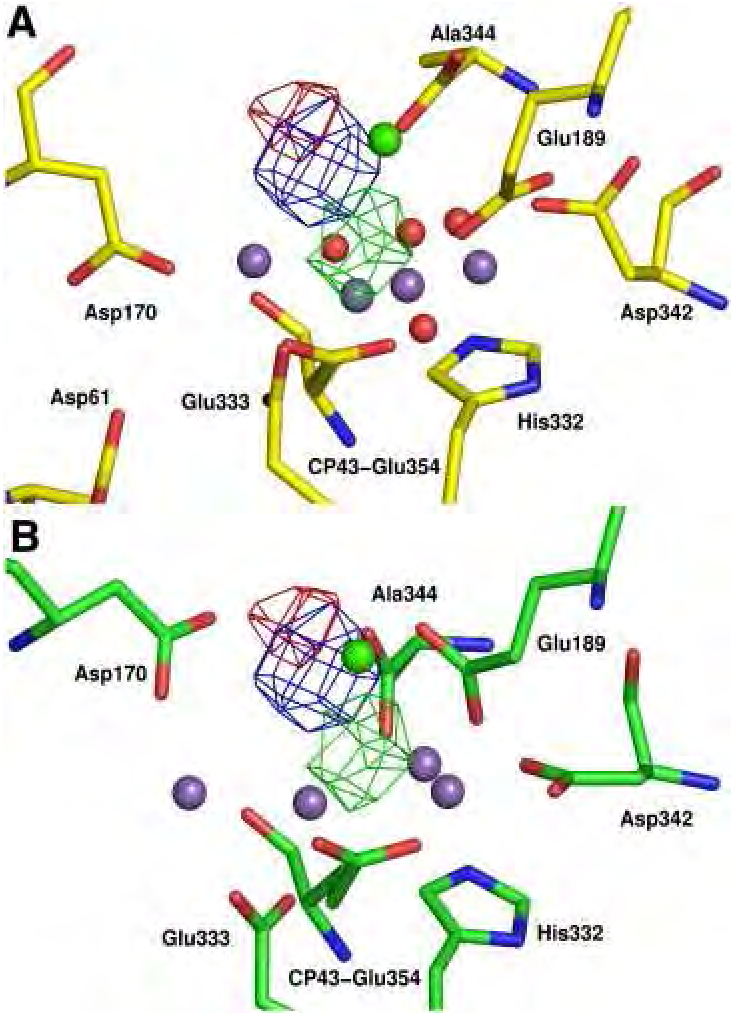






Boussac et al 2005

Location of Ca^{2+} using Sr^{2+} substituted PSII



Anomalous difference electron density maps above and below the Sr^{2+} K-edge.

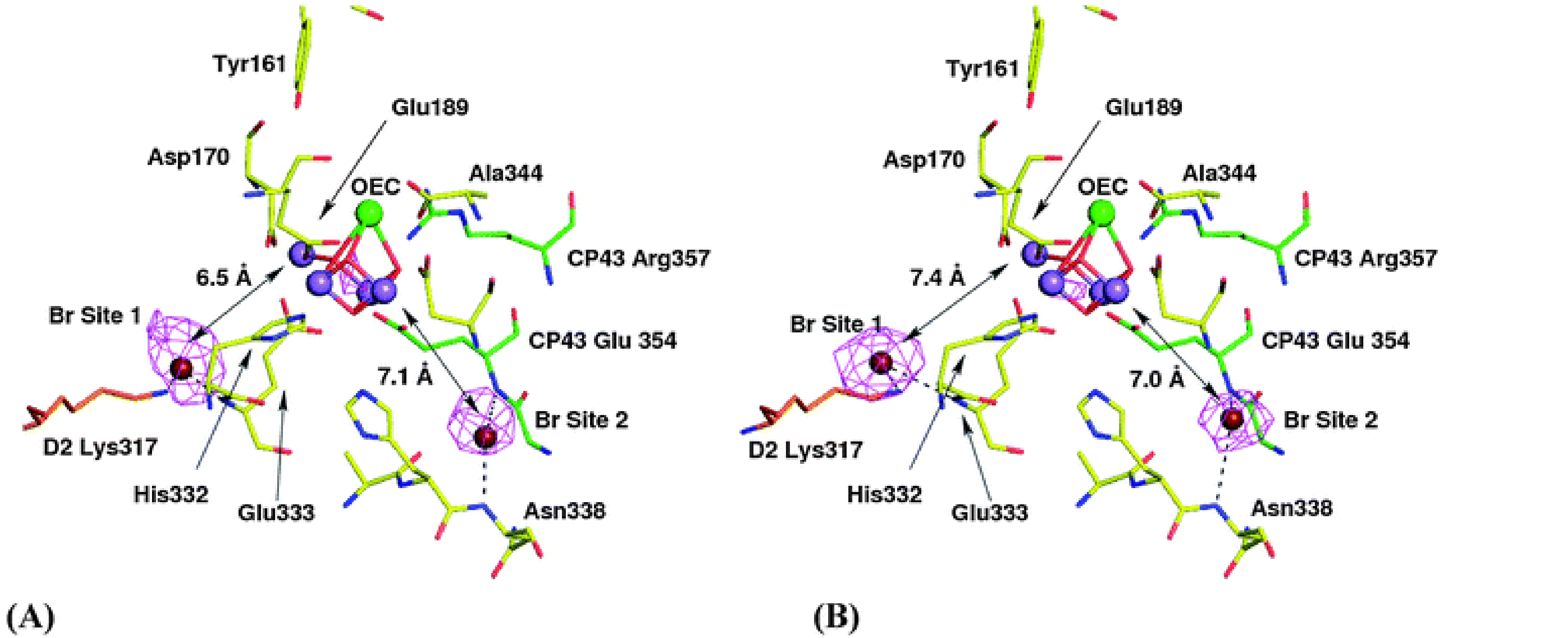
comparison with the Ca^{2+} position in the two refined crystal structures

Kargul et al 2007

Location of Cl⁻ binding sites

1) in crystals soaked Br⁻ medium

2) in crystals with Br⁻ present biosynthetically

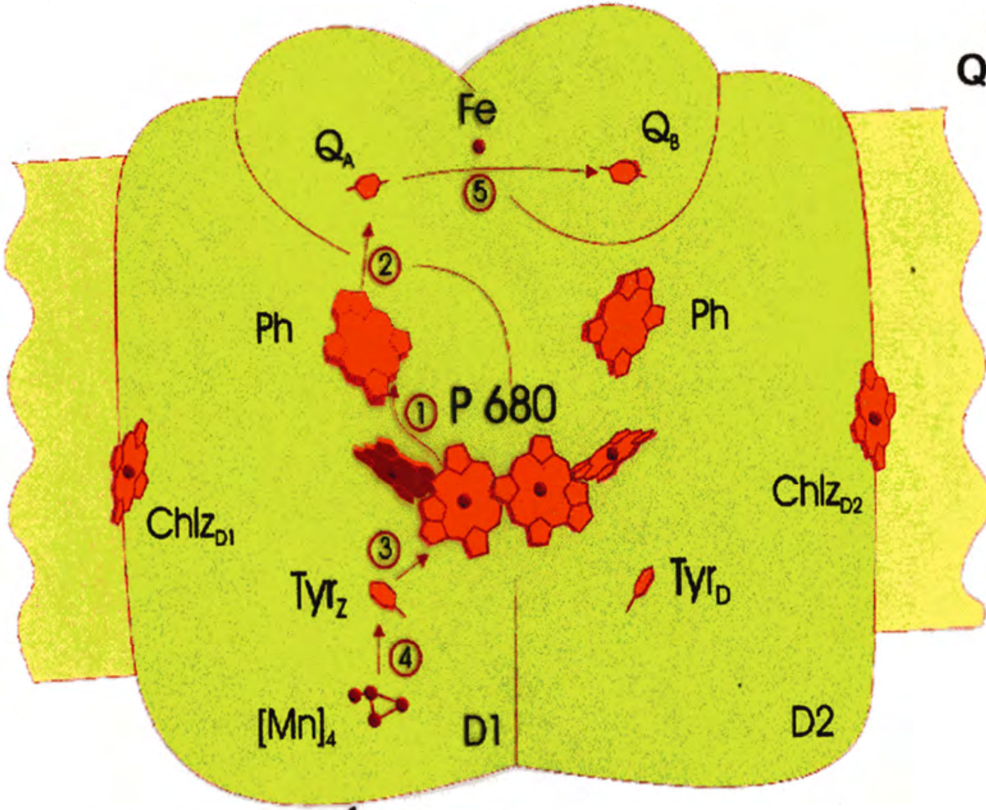


Murray et al 2008

The Problem:

we don't know how it works

$$Q \xrightarrow{e^-} Q^- \xrightarrow{e^-,\ 2H^+} QH_2$$

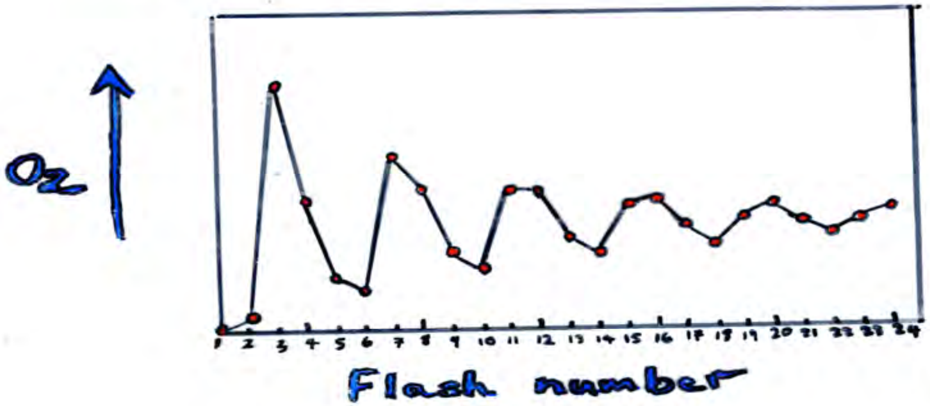


4 electrons

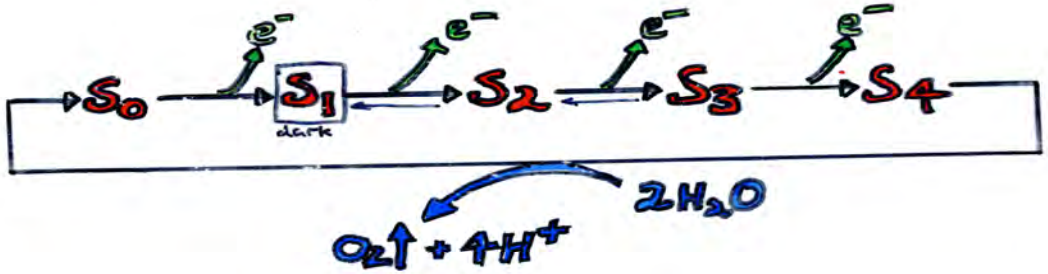
water → protons oxygen

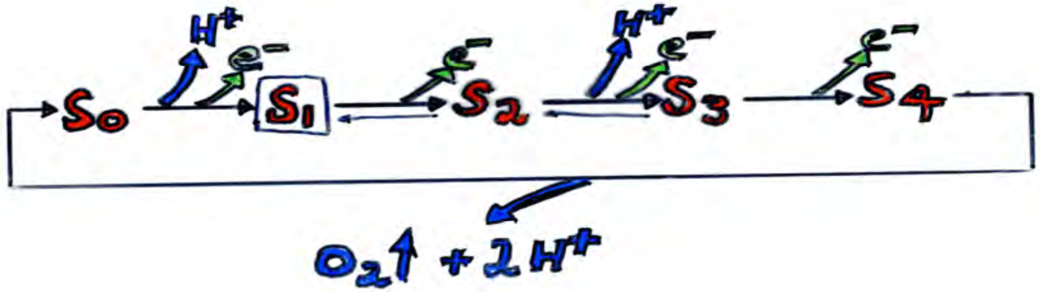
$2H_2O$ → $4H^+$ O_2

O_2 evolution & the model

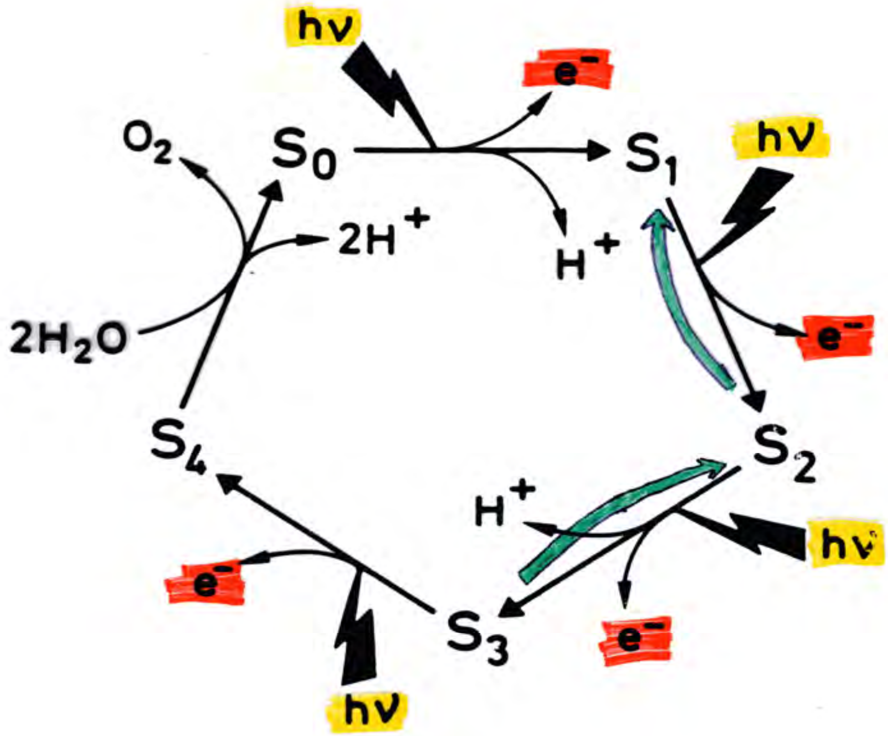


Kok et al 1970



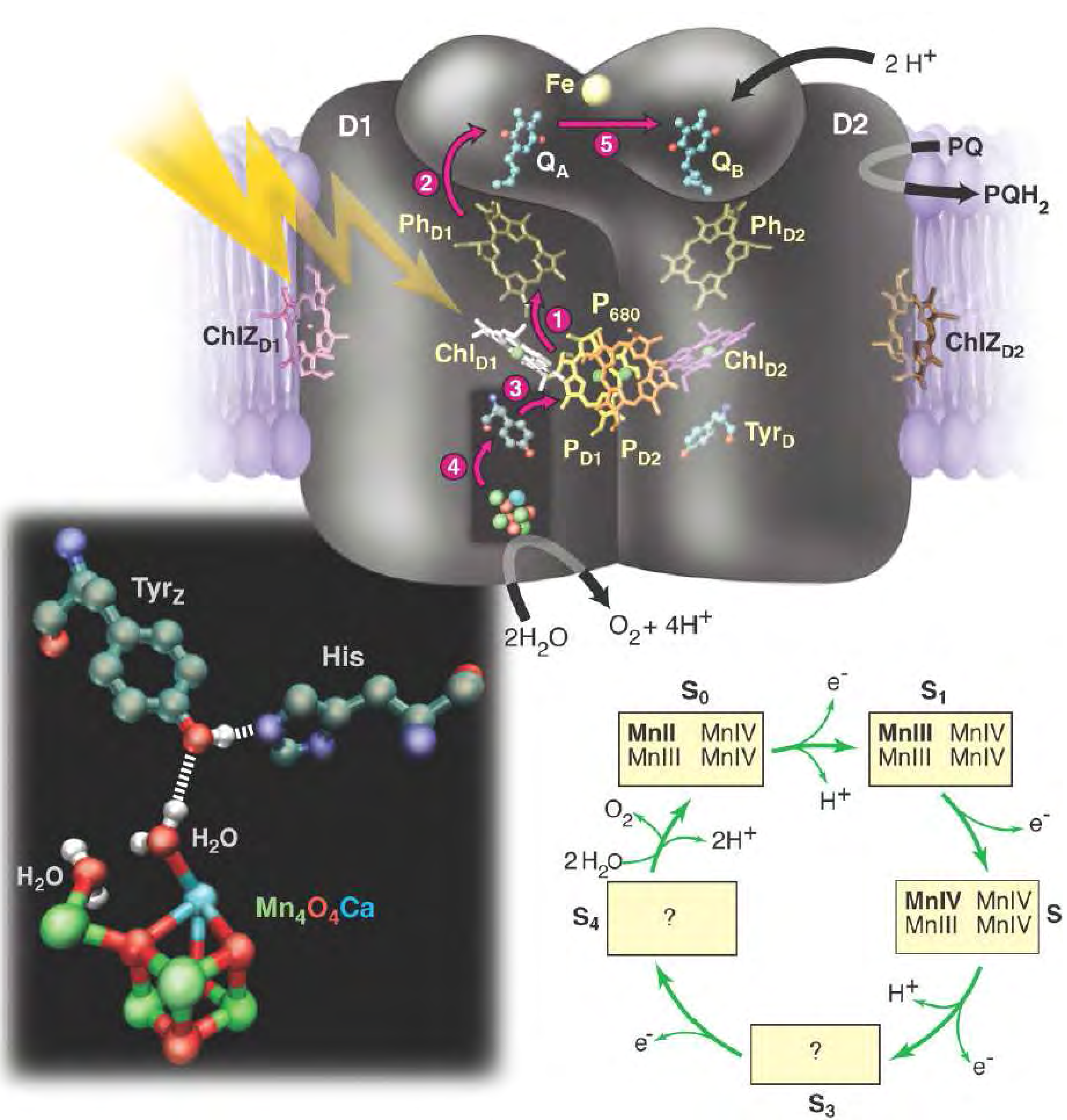


Charge accumulation: the kinetic model



notes: - 100% S_1 is present in the dark after a long dark-time.

- illumination at 200K results in almost quantitive formation of S_2 from S_1. All other S state reactions are inhibited at 200K.



2 H^+
Fe
D1
D2
Q_A
Q_B
PQ
PQH_2
Ph_{D1}
Ph_{D2}
P_{680}
$ChlZ_{D1}$
Chl_{D1}
Chl_{D2}
$ChlZ_{D2}$
Tyr_D
P_{D1}
P_{D2}
1
2
3
4
5
$2H_2O$
$O_2 + 4H^+$
Tyr_Z
His
H_2O
H_2O
Mn_4O_4Ca
S_0
MnII MnIV
MnIII MnIV
S_1
MnIII MnIV
MnIII MnIV
e^-
H^+
e^-
MnIV MnIV
MnIII MnIV
S
H^+
e^-
?
S_3
e^-
S_4
?
O_2
$2H^+$
$2 H_2O$

when and where does substrate water bind?

Is amino acid radical chemistry involved?

when does water get oxidized?

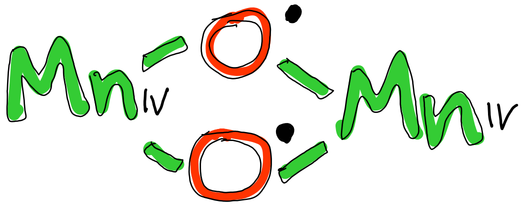
when is Mn oxidized?

what is the valence of the Mn?

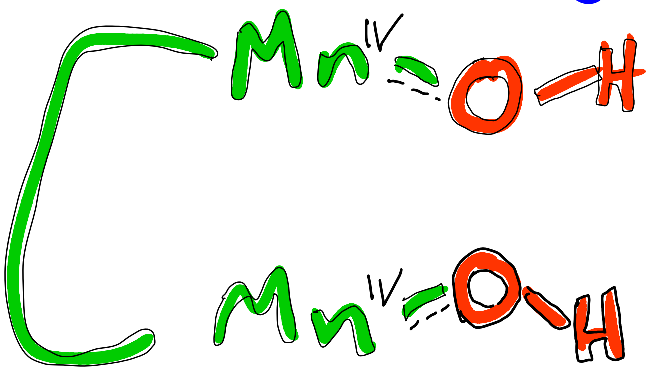
what kind of
chemistry is involved
in water oxidation?

Some mechanisms :

bridging oxo
radicals



nearby or
face to face
terminal ligands



one "hot" Mn
+ redox resevoir

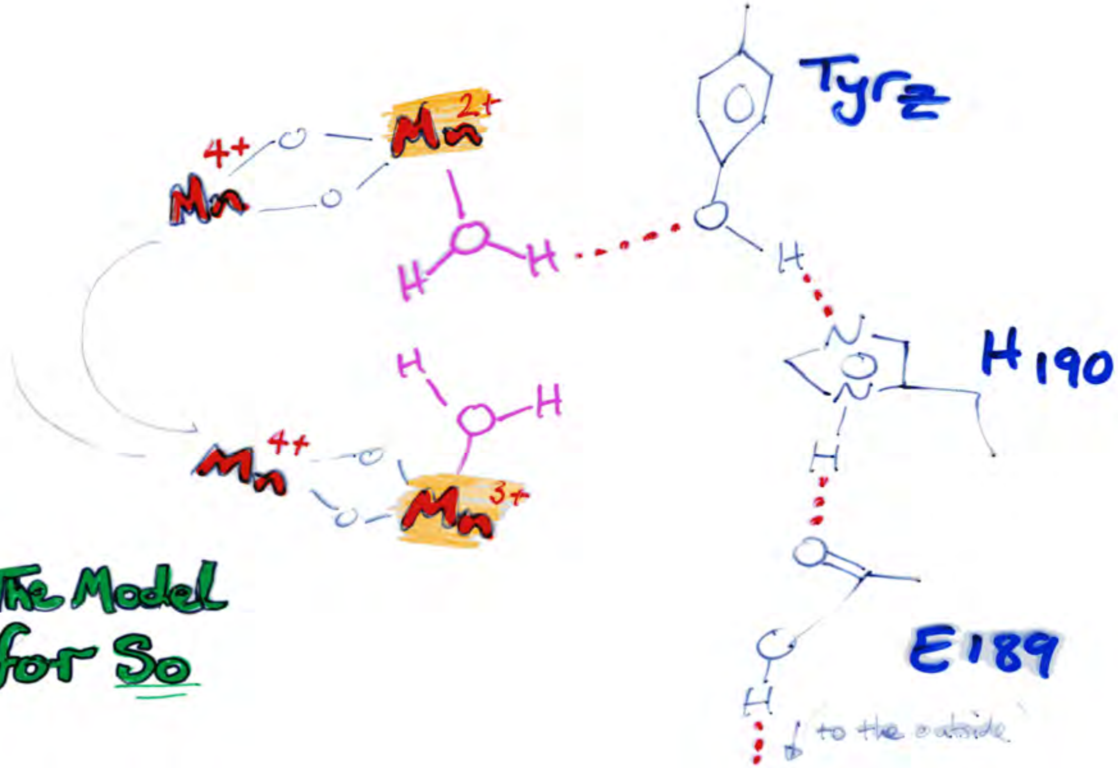
Metallo-radical Mechanism: 1 "The Babcock"

The main features:

1 Tyrosyl radical removes a hydrogen atom from water/Mn complex.

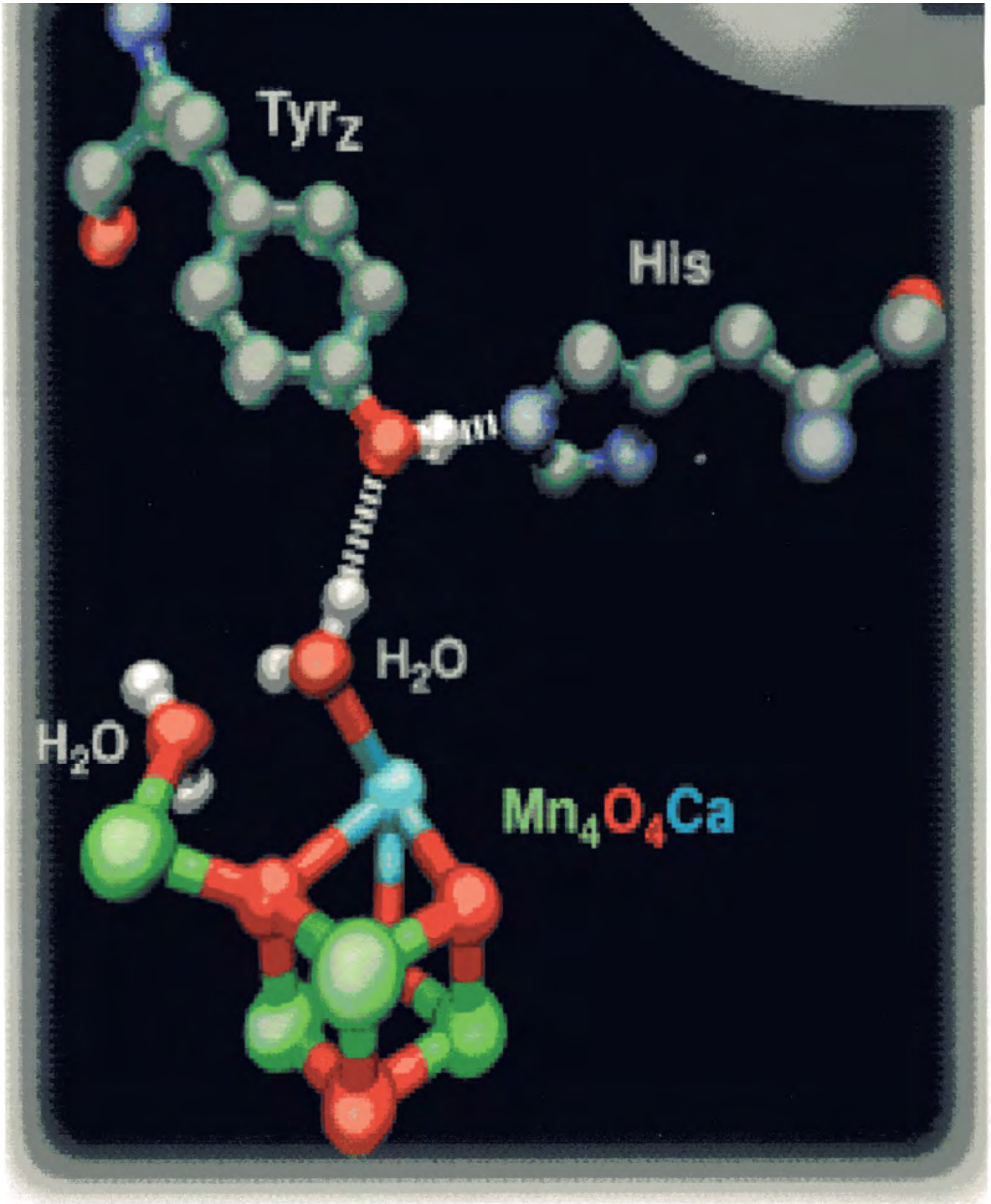
2 The S-state cycle is electroneutral on all steps

3 Terminal ligands oxidized



The Model for So

The cluster is close enough to Tyr$_Z$ to allow H bonding from cluster-bound substrate



The chemistry involved in water oxidation is still poorly defined

We need to find and study intermediates in the $S_3 \rightarrow S_4 \rightarrow S_0$ transition

Strategies for finding intermediates

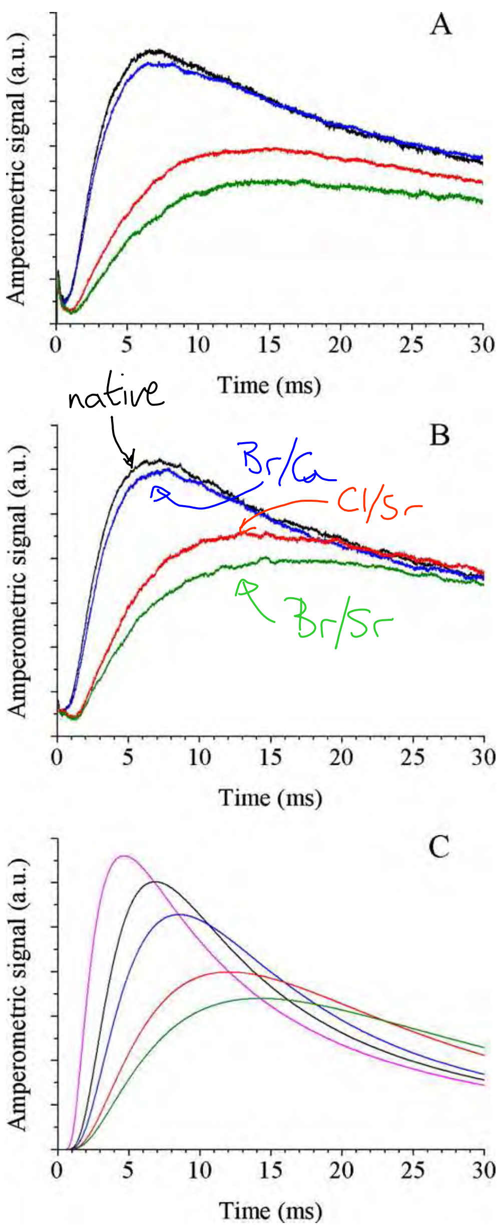
1 $[O_2]\uparrow$ $\quad 2H_2O \underset{\nwarrow 2e}{\overset{\nearrow 2e}{\rightleftharpoons}} H_2O_2 + 2H^+ \underset{\nwarrow 2e}{\overset{\nearrow 2e}{\rightleftharpoons}} O_2 + 4H^+$

2 time resolution, electronic absorption, Xray abs,

3 trapping at low temp

4 modifications → mutants
→ other modifications

The effect of Cl^-/Br^- and Ca^{2+}/Sr^{2+} replacement on the rate of O_2 release



Kinetics of the oxygen release measured after the third flash on CaCl-thylakoids (black), CaBr-thylakoids (blue), SrCl-thylakoids (red), and SrBr-thylakoids (green)

O_2 release gets slower when Br^- and Sr^{2+} replace the native Cl^- and Ca^{2+}

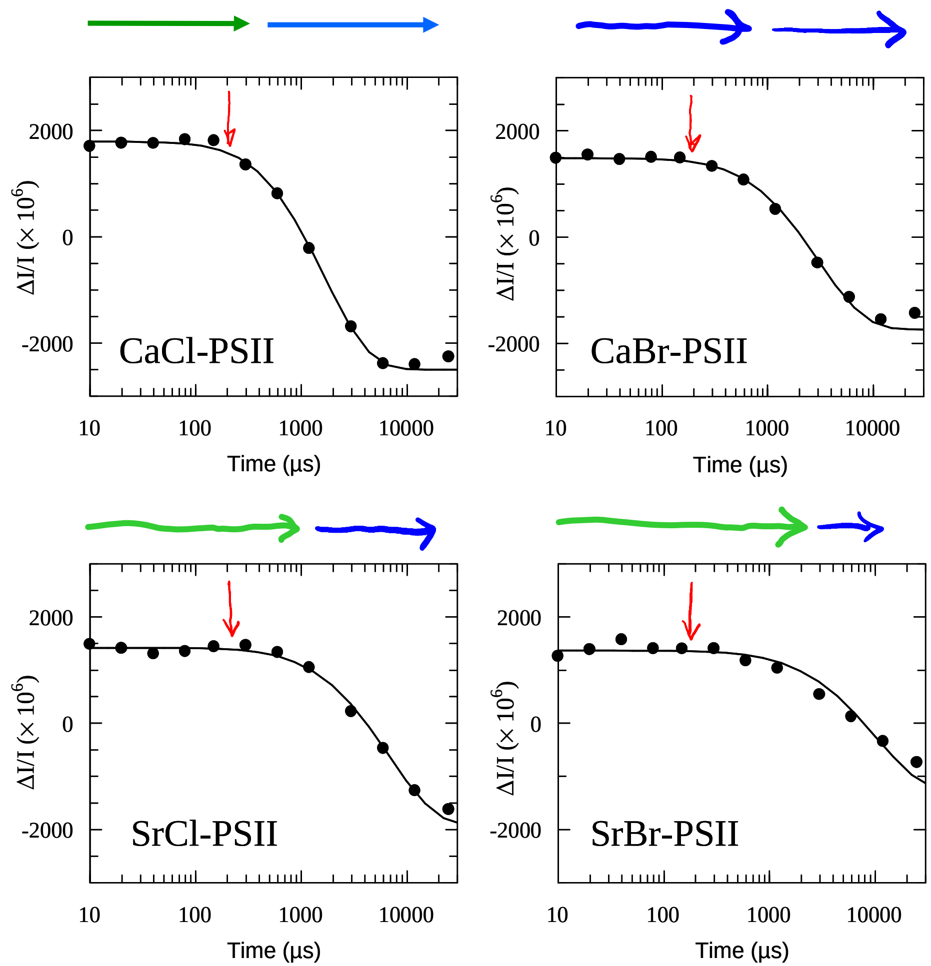
$t_{1/2} < Cl^-/Ca^{2+} < Br^-/Ca^{2+} < Cl^-/Sr^{2+} < Br^-/Sr^{2+}$

Ishida, N. et al. J. Biol. Chem. 2008;283:13330-13340

The lag phase in the $S_3TyrZ^\bullet$ to $S_0TyrZ + O_2$ transition

ΔA 350 nm: Koike et al. 1987 BBA, 893, 524.
ΔA 295 nm: Rappaport et al. 1994 BBA, 1184, 178.
EPR oxymetry: Razeghifard and Pace 1999 Biochemistry, 38, 1252
Time resolved X-ray absorption: Haumann et al. 2005 Science, 310, 1019.

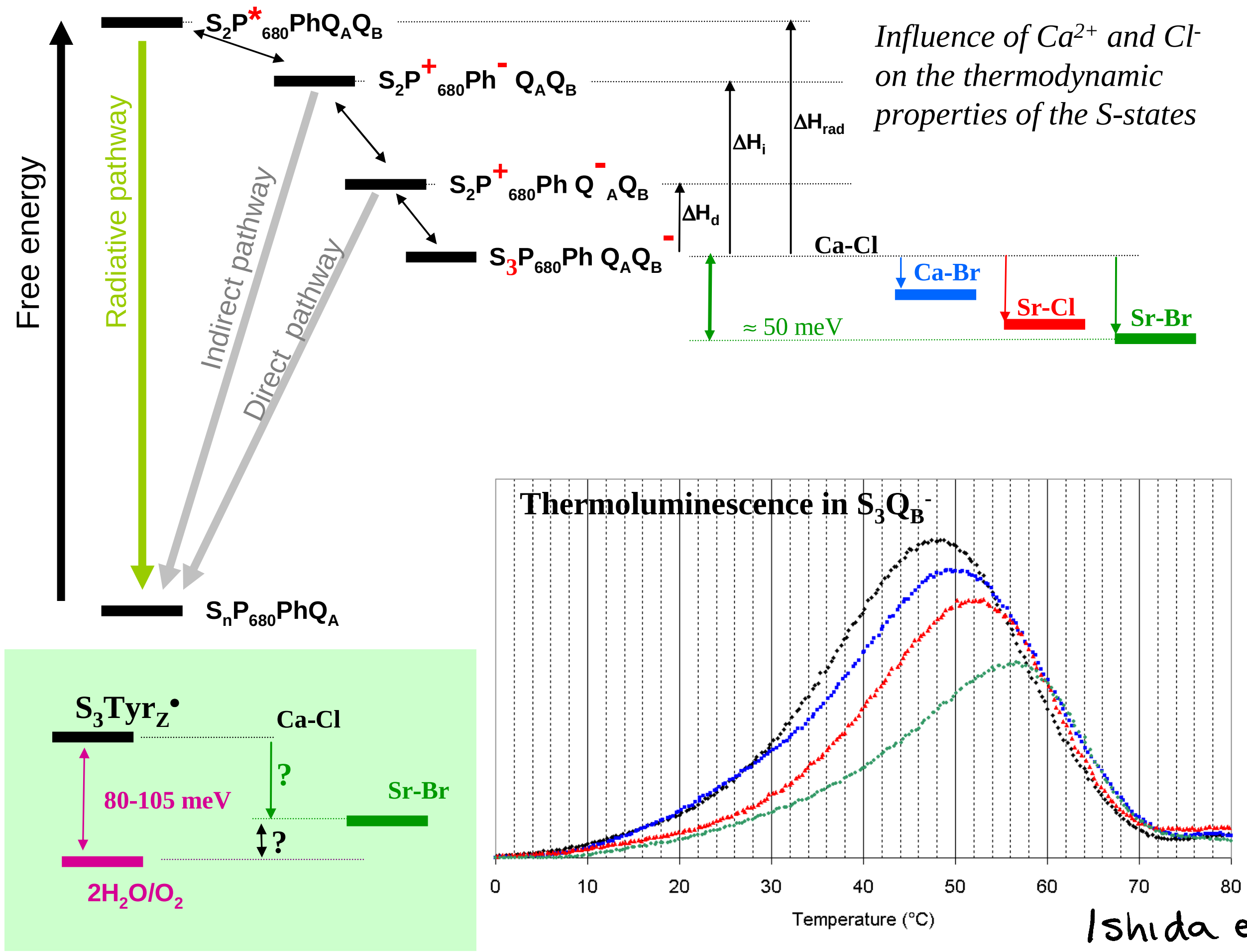
$S_3TyrZ^\bullet \rightarrow (S_3TyrZ^\bullet)' \rightarrow S_0TyrZ$



	$t_{1/2}$	
	lag (µs)	$S_3Tyr_Z^\bullet \rightarrow S_0Tyr_Z$ (ms)
CaCl	115	1.1
CaBr	140	2.1
SrCl	210	4.8
SrBr	230	7.2

Ishida et al 2008

Charge recombination luminescence indicates S_3 is more stable when Br and Sr are present



Ishida et al 2008

Implications: smaller driving force on the water oxidation step?

Br^-/Sr^{2+} sample good for the hunt for intermediates

Ishida et al 2008

The cofactors Ca^{2+} and Cl^- contribute in the tuning of the high driving force required to split water. In PSII in which Ca^{2+} and Cl^- are biosynthetically substituted for Sr^{2+} and Br^-, respectively, the free energy level of the S_3 state decreased. This can be detected by a thermoluminescence experiment where the temperature at which the $S_3Q_B^-$ charge recombination occurs is indicative of the energy gap, ΔH_{rad}, between the states $S_3P680Q_B^-$ and $S_2P680^*Q_B$. Since the SrBr-PSII is fully competent in O_2 evolution and if the decrease by □ 50 meV of the free energy level in the S_3 state in SrBr containing PSII when compared to the CaCl containing PSII is true and persists in the S_3Tyr_Z□ state, the 80-105 meV found earlier (1, 2) as the driving force available to split water could be slightly underestimated.

1) Clausen, J., Junge, W., Dau, H., Haumann, M. (2005) *Biochemistry* 44, 12775-12779.

2) Vos, M. H., van Gorkom, H. J., and van Leeuwen, P. J. (1991) *Biochim. Biophys. Acta* 1056, 27-39.

meanwhile - - - —

back at the alternative enegy front line

First aim:

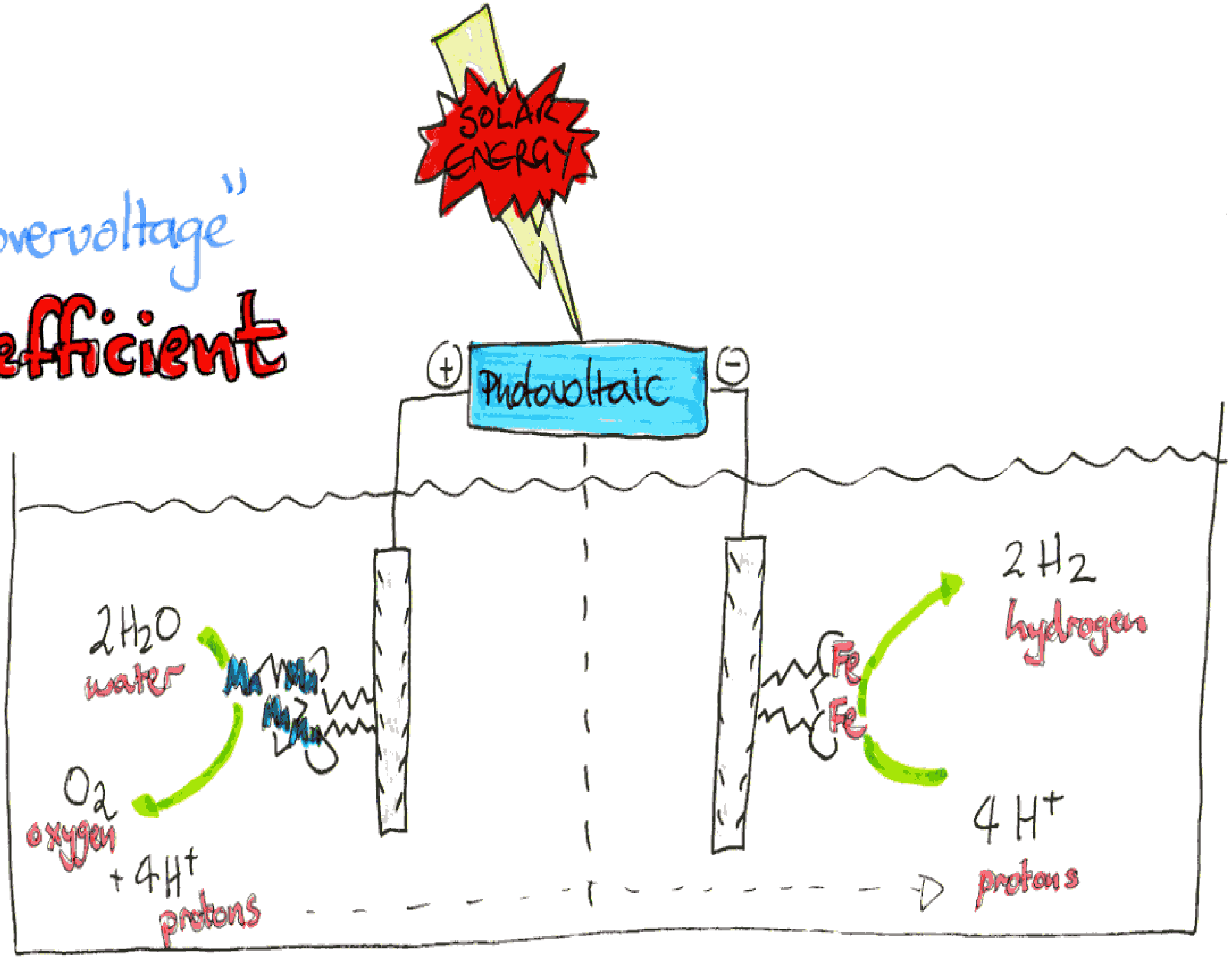
to design and make new catalysts inspired by

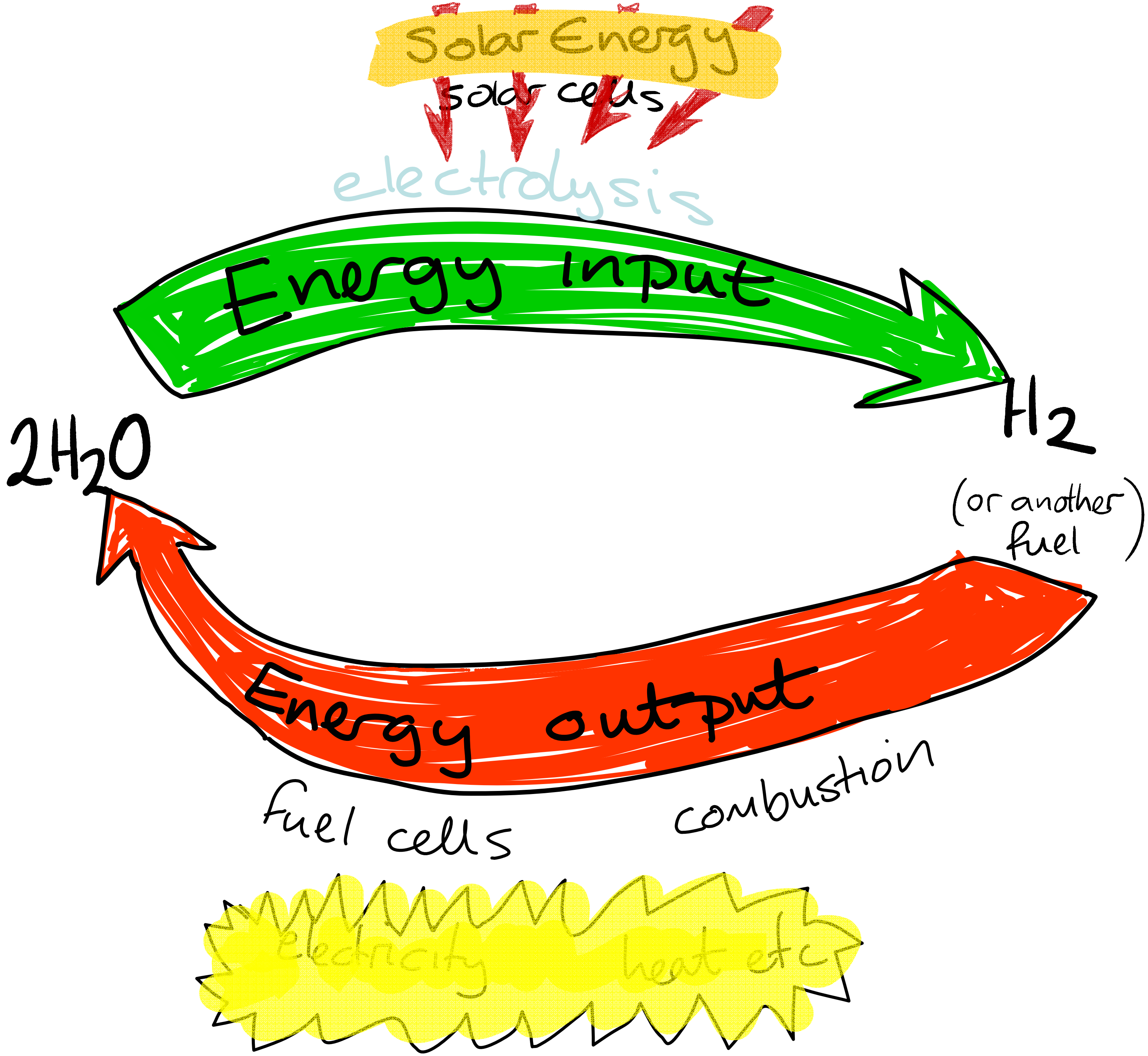
1. the water splitting enzyme
2. hydrogenases

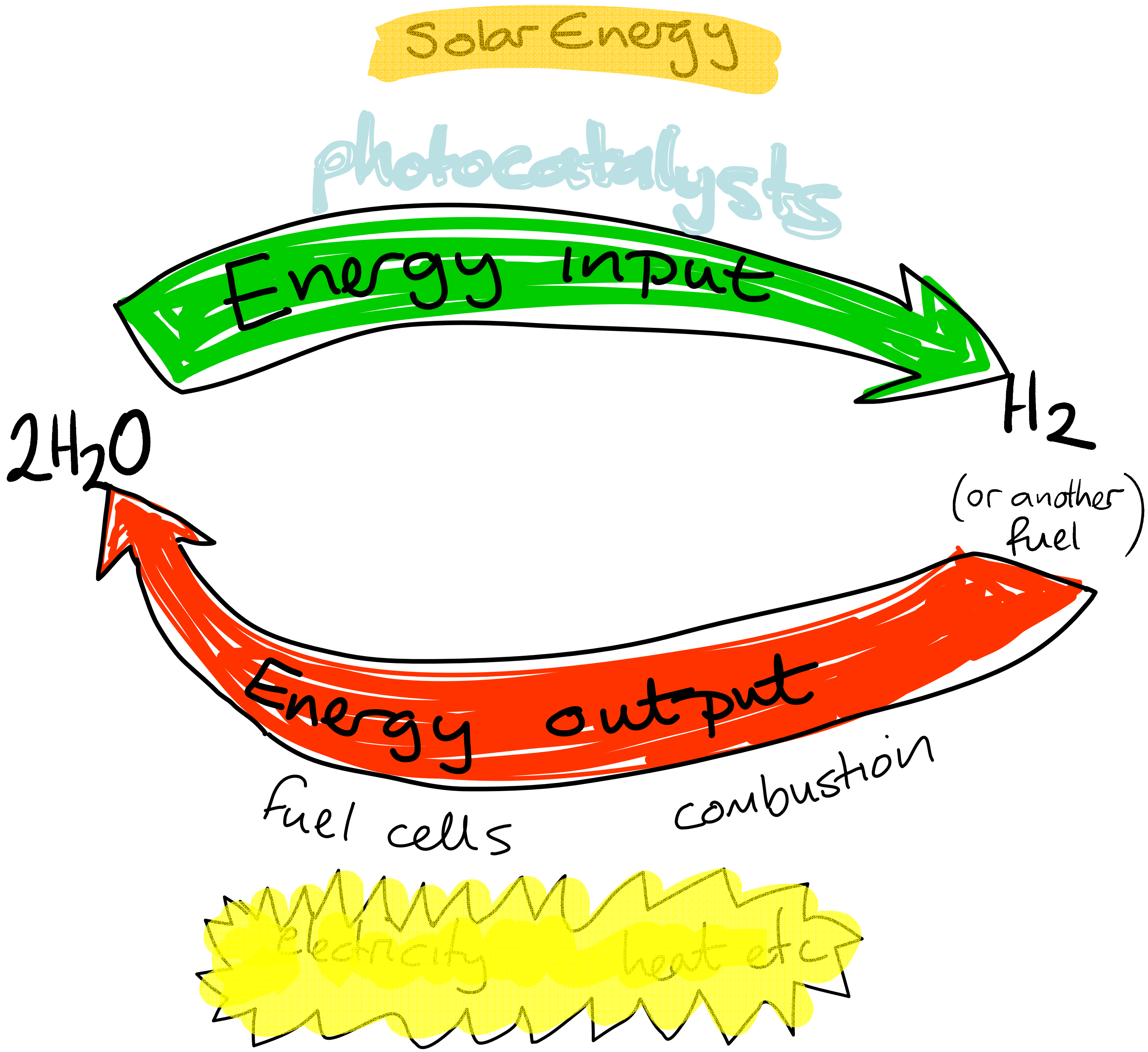
Can bioinspired catalysts improve efficiencies?

small "overvoltage"

more efficient

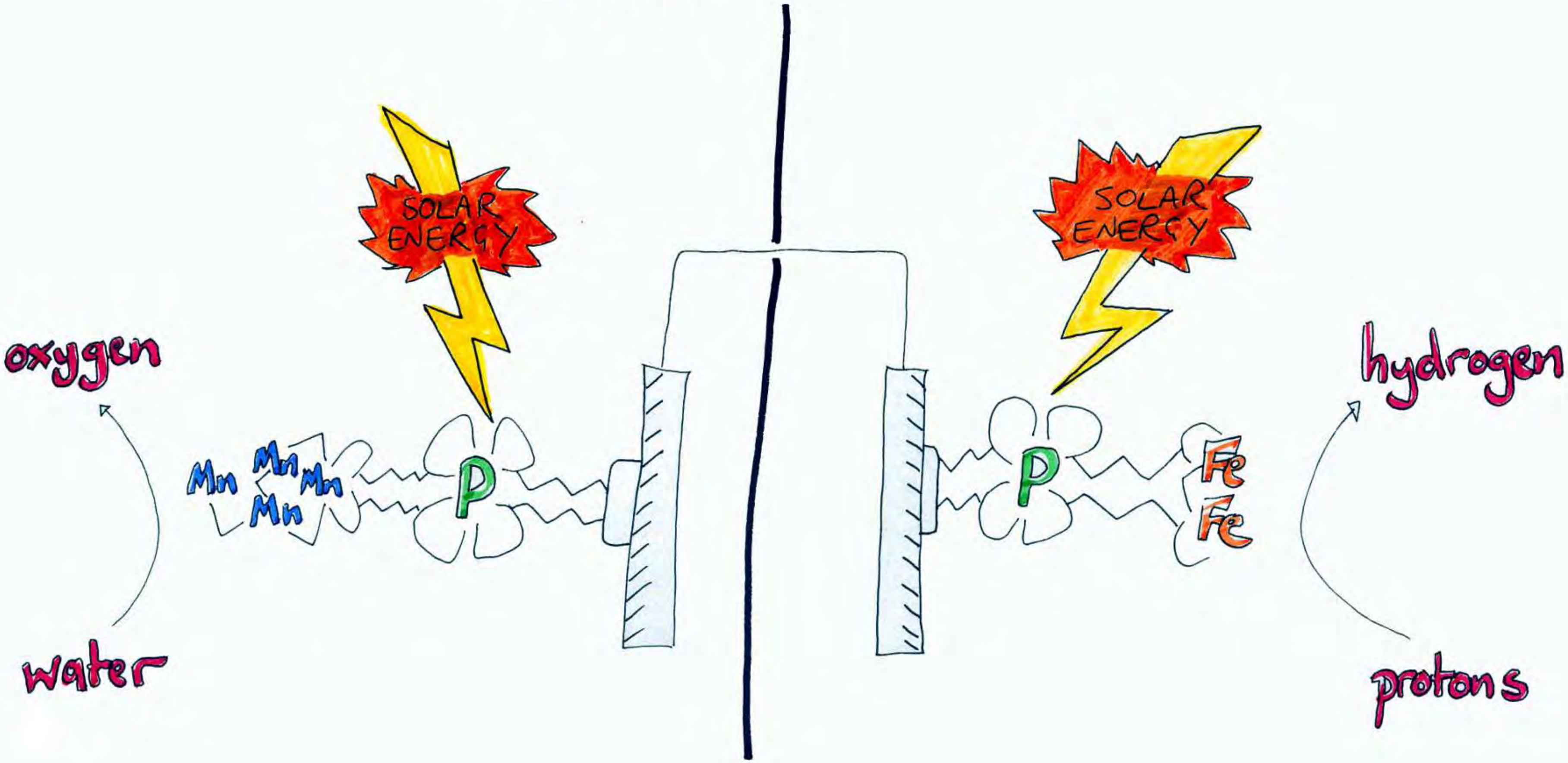



Solar Energy
solar cells
electrolysis
Energy input
H_2
(or another fuel)
$2H_2O$
Energy output
fuel cells
combustion
electricity
heat etc

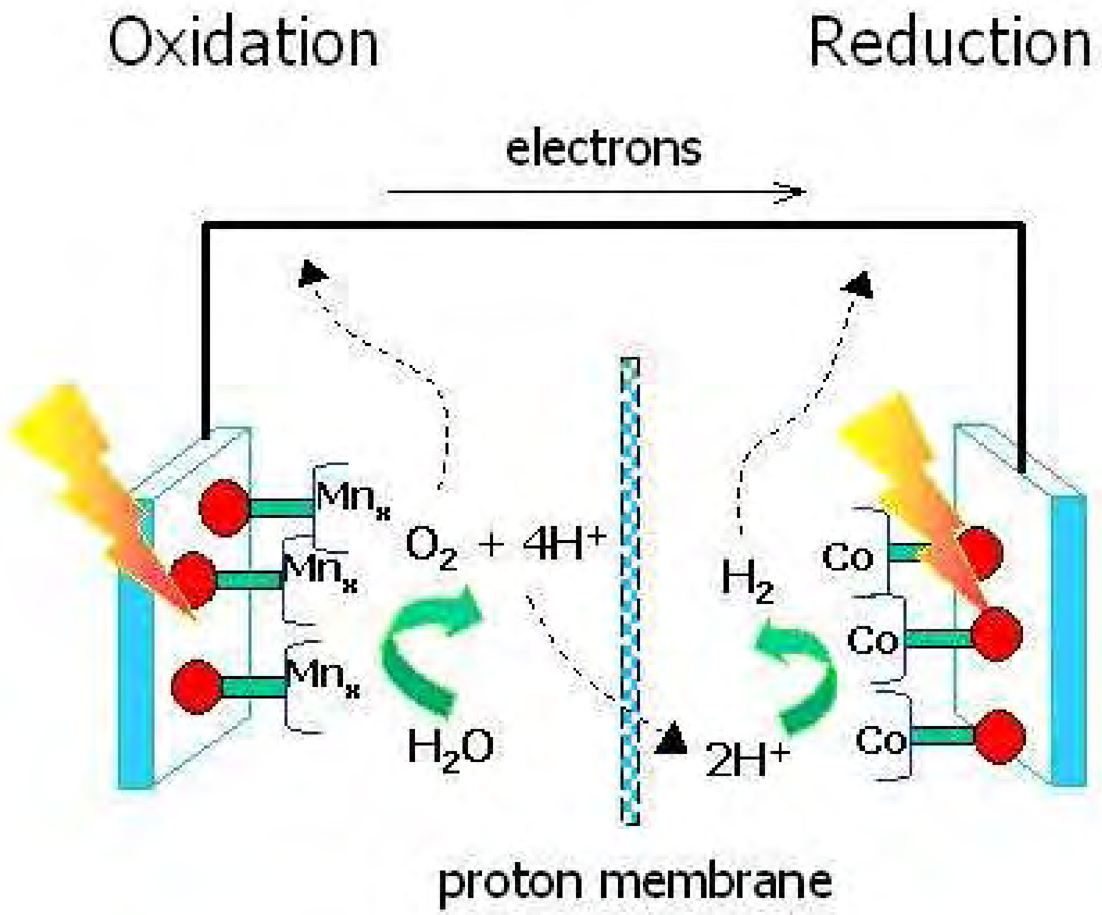


Solar Energy
photocatalysts
Energy input
2H2O
H2
(or another fuel)
Energy output
fuel cells
combustion
electricity
heat etc

Imaginary Artificial water photolysis cell based on photosynthetic electron transfer



Towards a photocatalytic cell

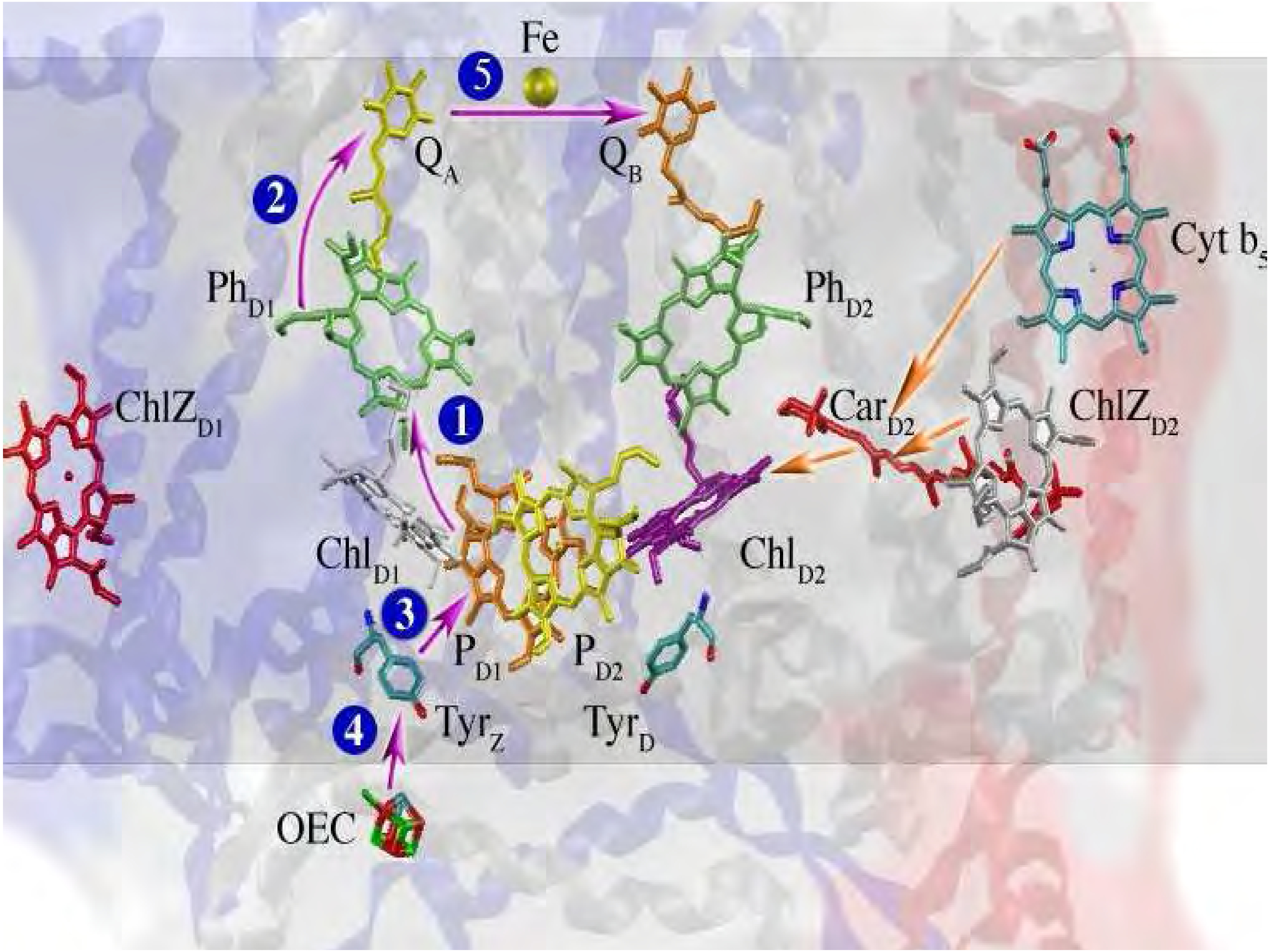


Second aim:

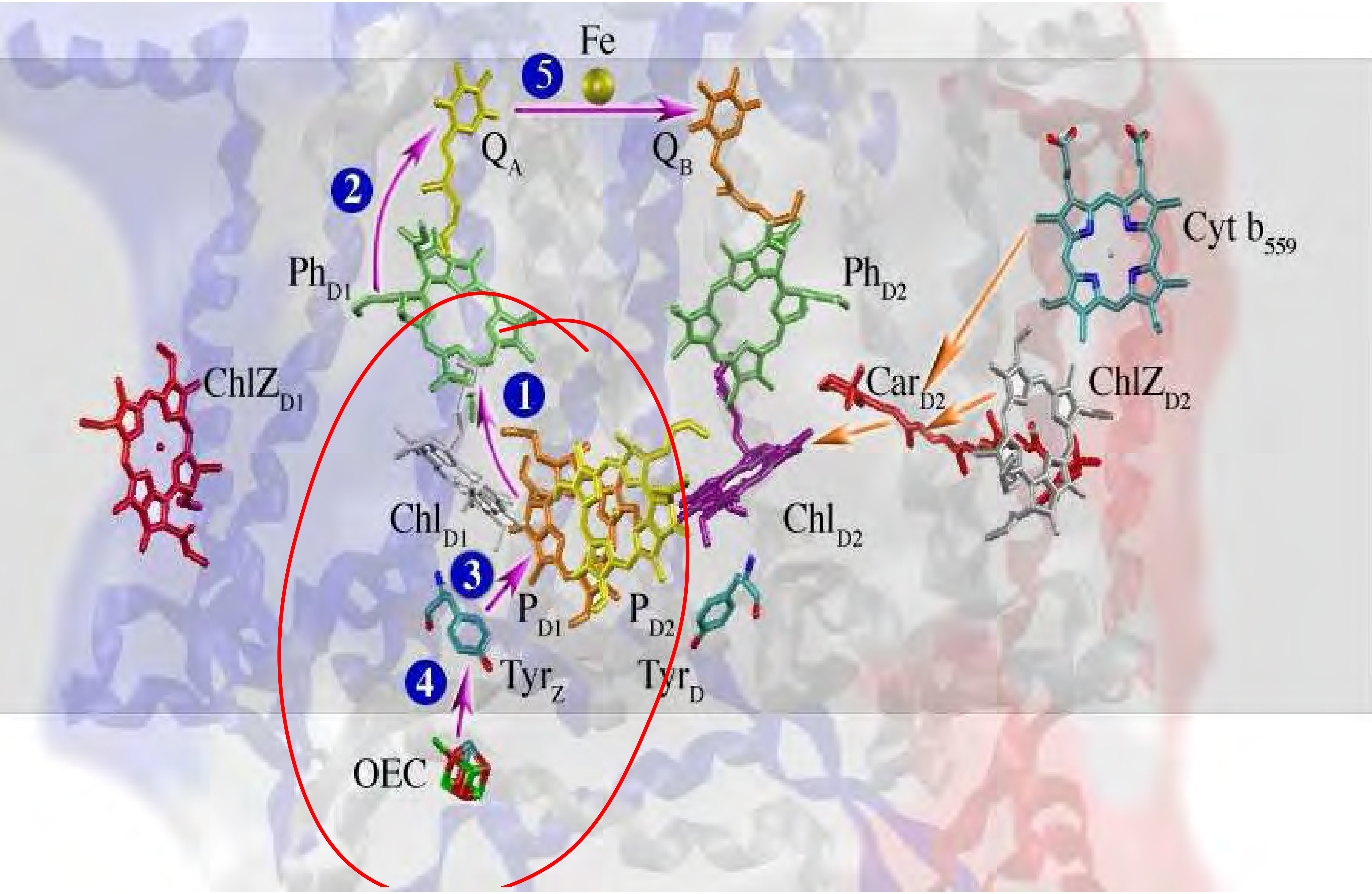
to design and make photo catalysts based on

1 the water splitting enzyme

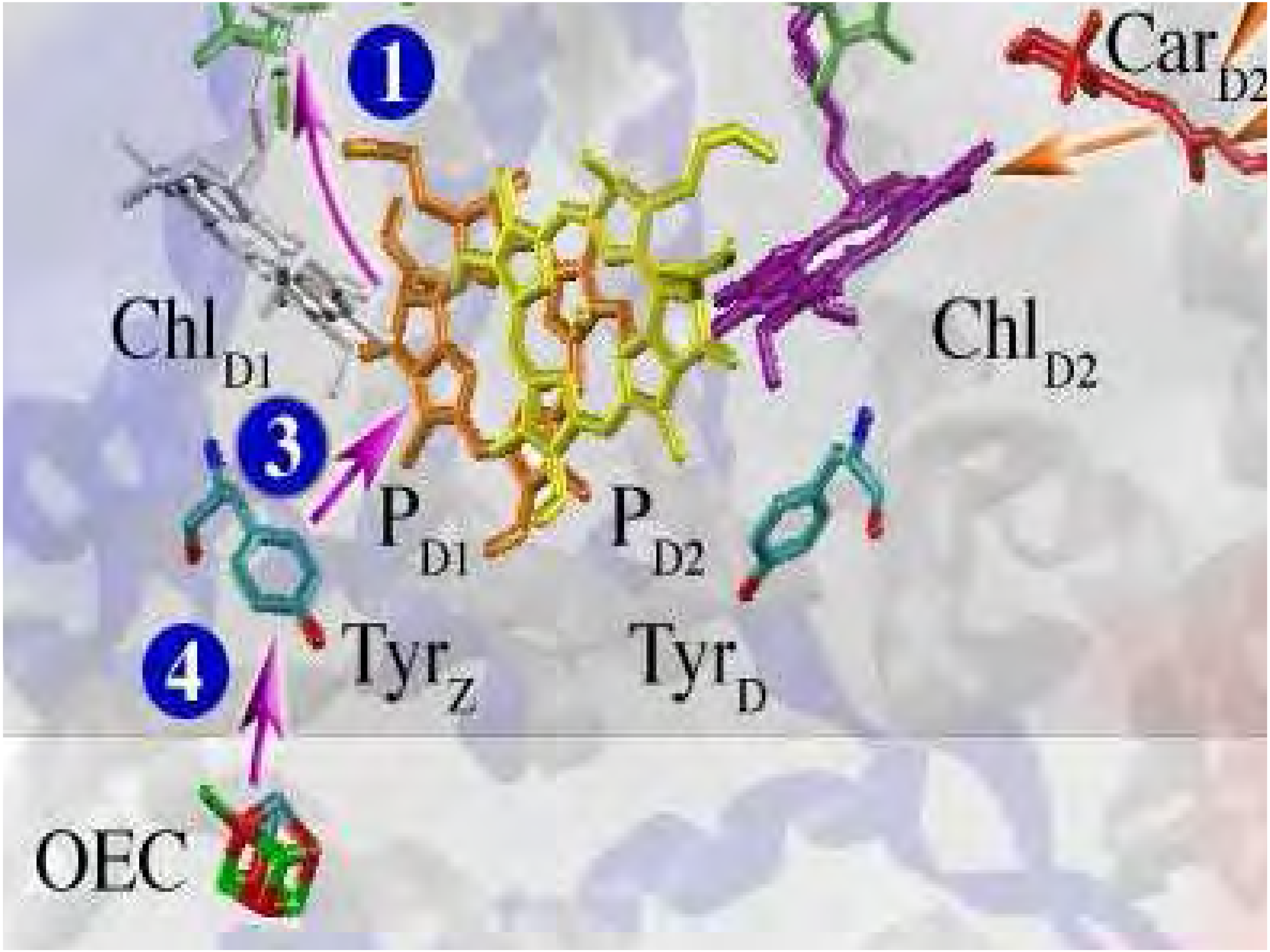
(2 hydrogenases)



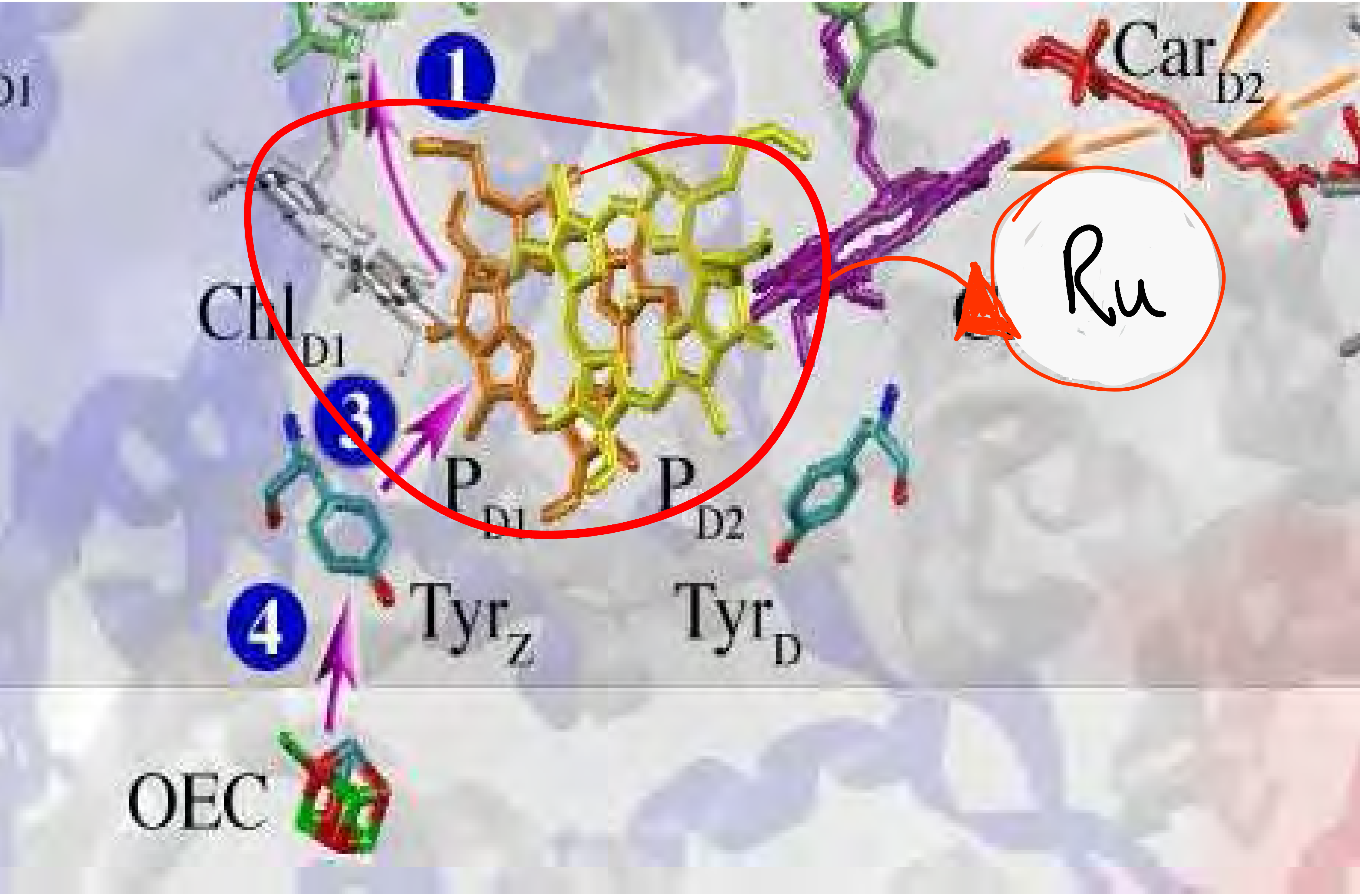
Fe
5
Q_A
Q_B
2
Cyt b_5
Ph_{D1}
Ph_{D2}
$ChlZ_{D1}$
1
Car_{D2}
$ChlZ_{D2}$
Chl_{D1}
Chl_{D2}
3
P_{D1}
P_{D2}
4
Tyr_Z
Tyr_D
OEC

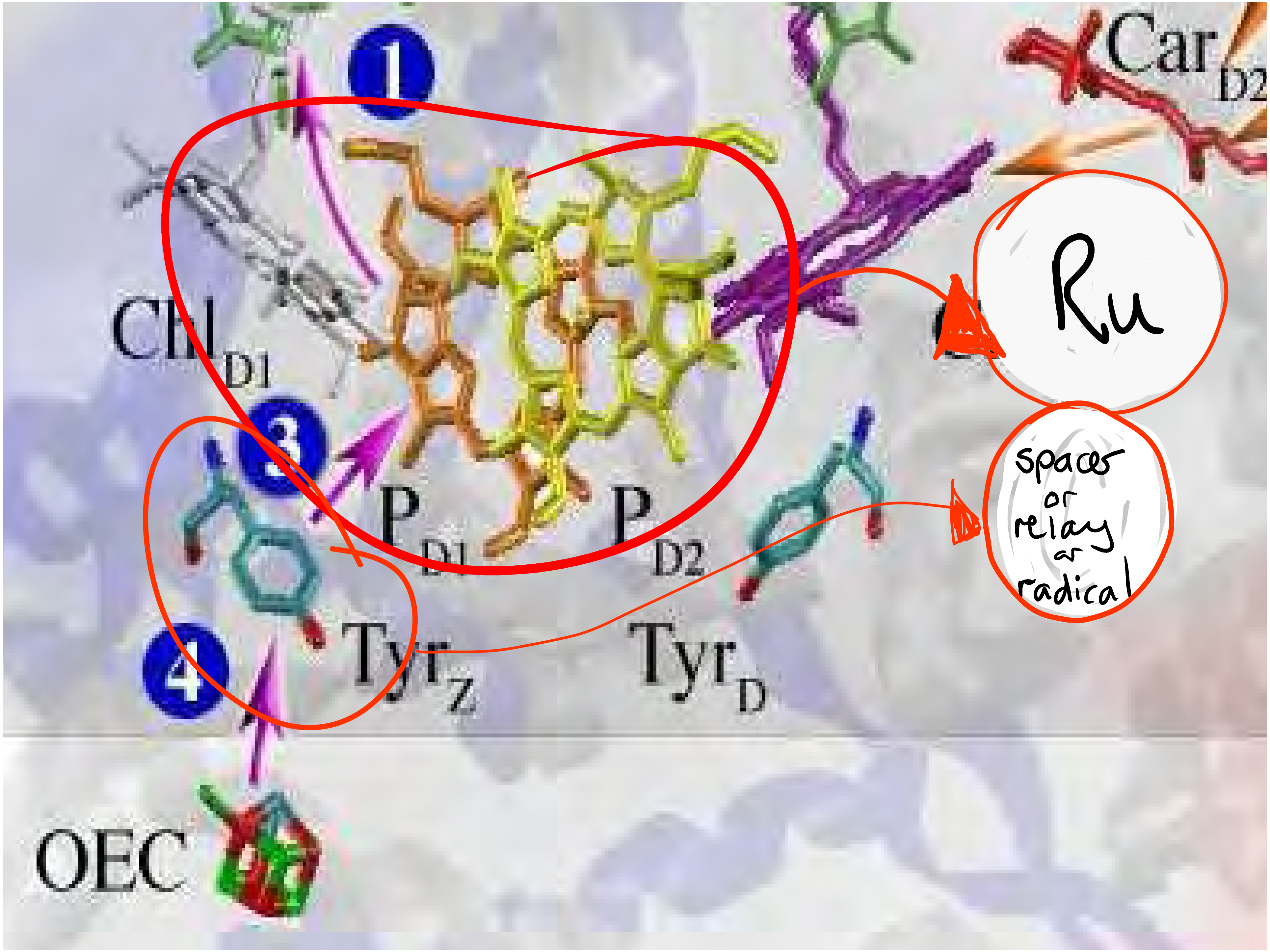


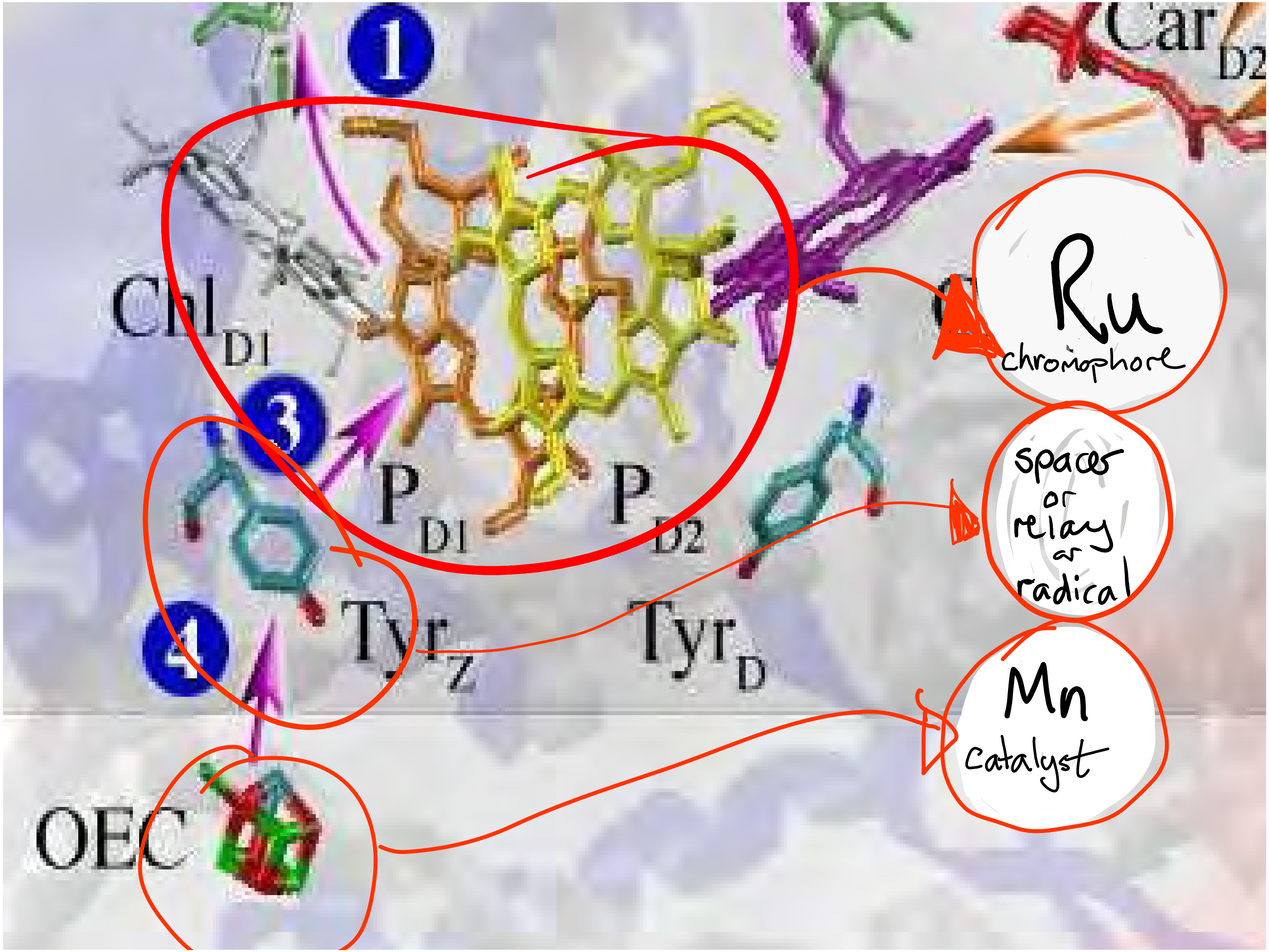
Fe
5
Q_A
Q_B
2
Cyt b559
Ph_D1
Ph_D2
ChlZ_D1
1
Car_D2
ChlZ_D2
Chl_D1
Chl_D2
3
P_D1
P_D2
Tyr_Z
Tyr_D
4
OEC



Car D2
1
Chl D1
Chl D2
3
P D1
P D2
Tyr Z
Tyr D
4
OEC

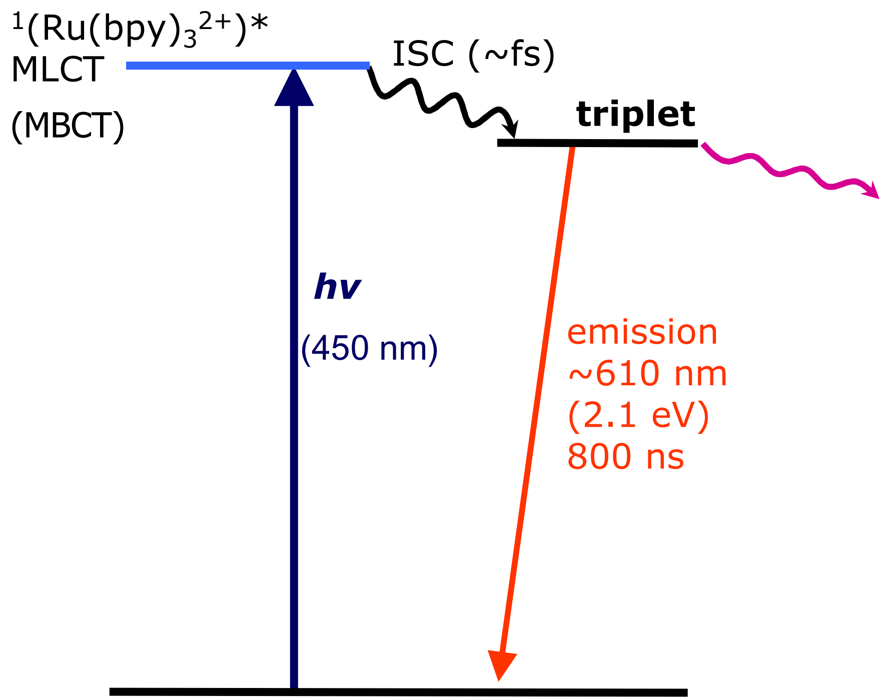

Car D2
1
Chl D1
3
P D1
P D2
Ru
4
Tyr Z
Tyr D
OEC


1
Car D2
Ru
Chl D1
3
P D1
P D2
spacer
or
relay
or
radical
4
Tyr Z
Tyr D
OEC

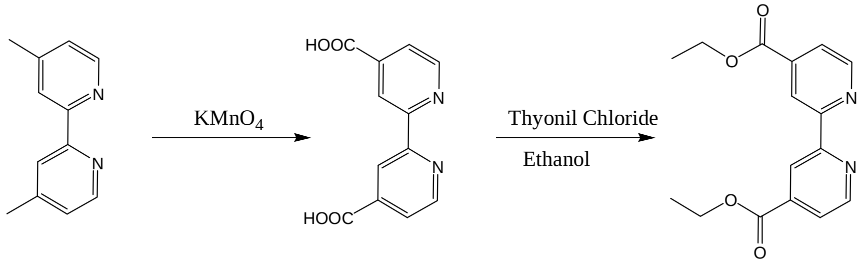

1
Car D2
Chl D1
3
P D1
P D2
4
Tyr Z
Tyr D
OEC
Ru
chromophore
spacer
or
relay
or
radical
Mn
catalyst

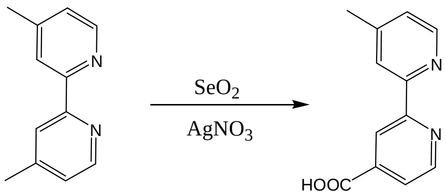
Photoactive center

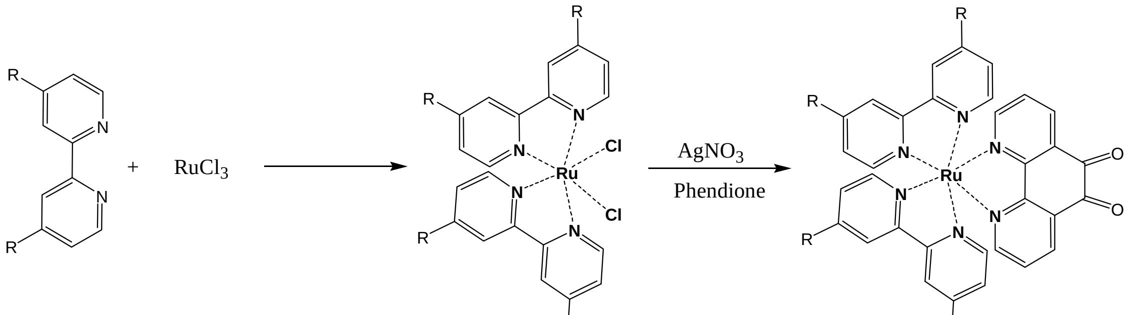
- Based on Ruthenium tris(bipyridyl) complexes
- Absorb light in the visible region MLCT~ 460 nm
- Emission at 610 nm
- Lifetimes around micro second
- Oxidation potential around 1.3 V
- Easily modified to change properties



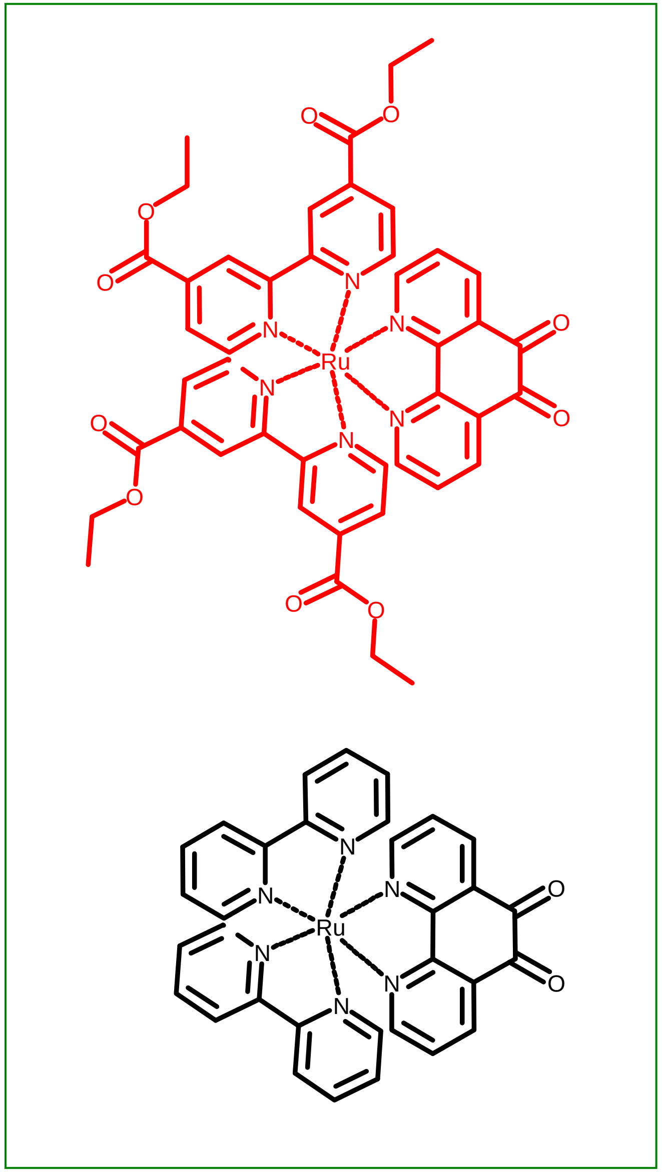
Photoactive center

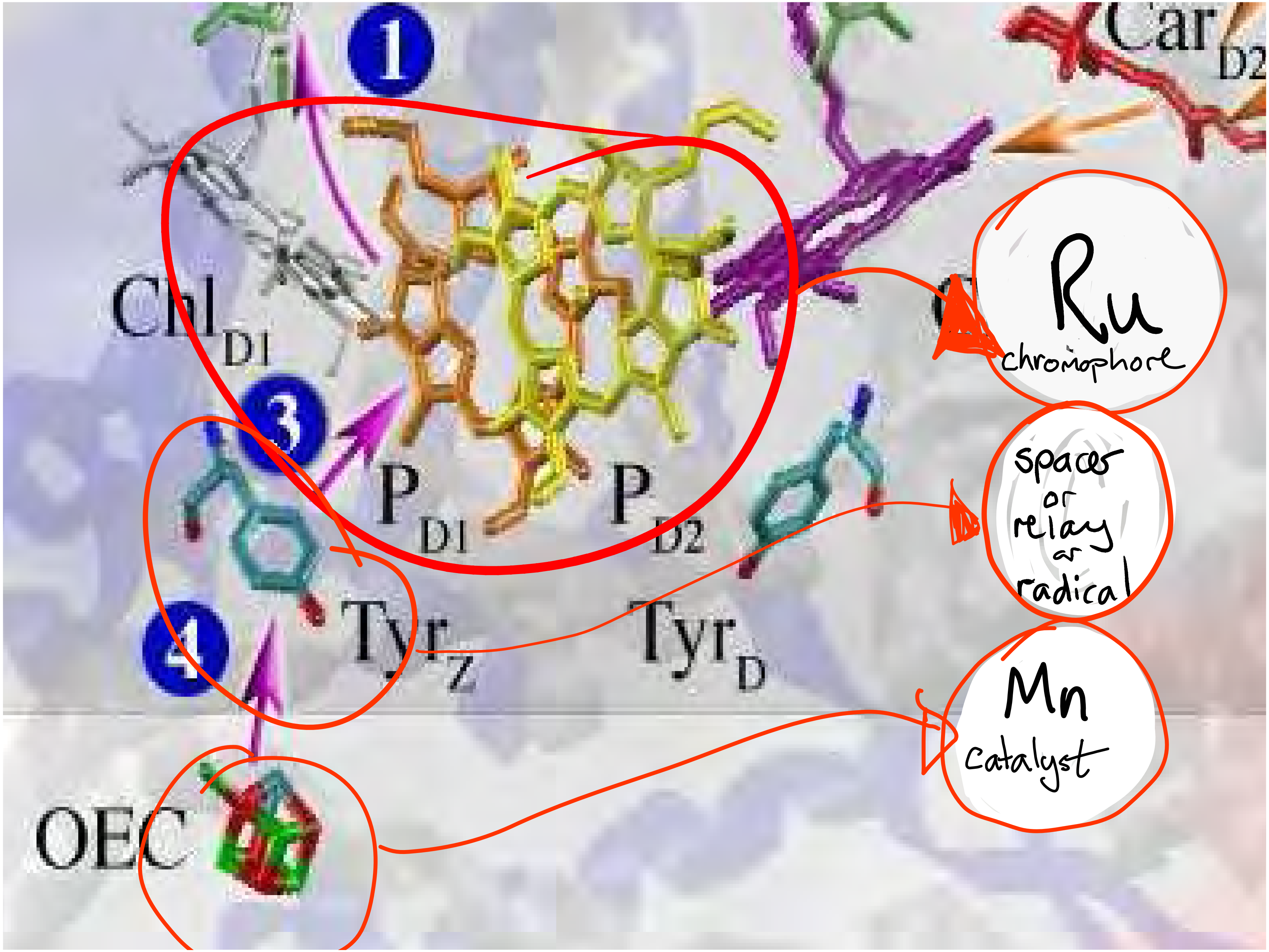






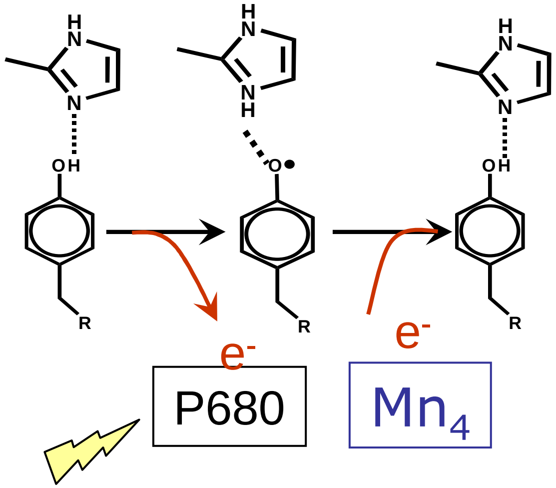
R = H, Ethyl ester, carboxylic acid

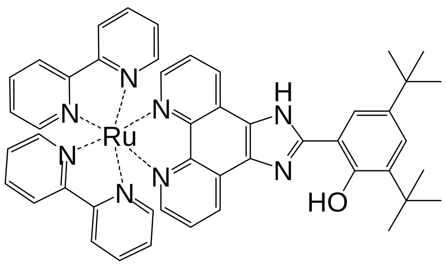


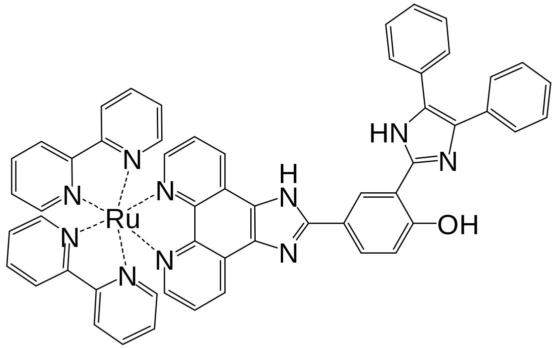

1
3
4
Chl D1
P D1
P D2
Tyr Z
Tyr D
OEC
Car D2
Ru
chromophore
spacer
or
relay
or
radical
Mn
catalyst

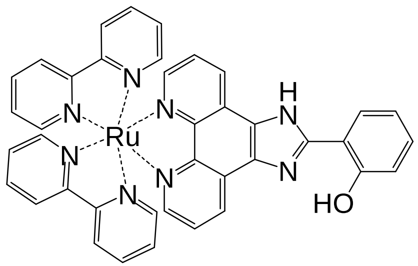
Electron relay

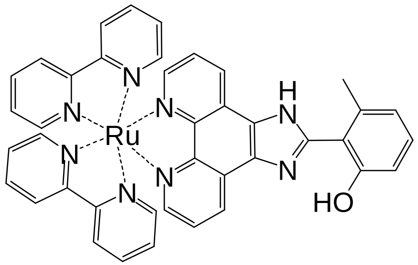
- Effect of structural changes on chemical properties
  - Distance, angle, oxidation potential

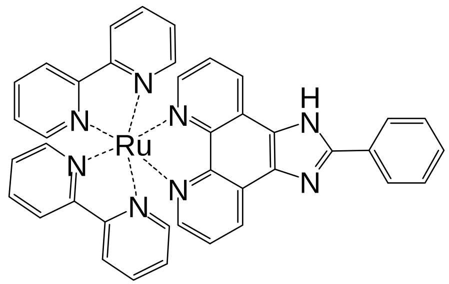


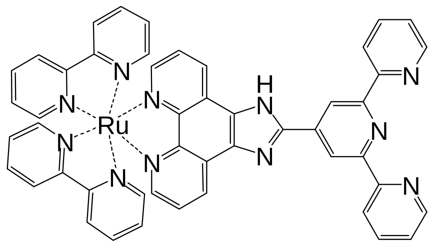


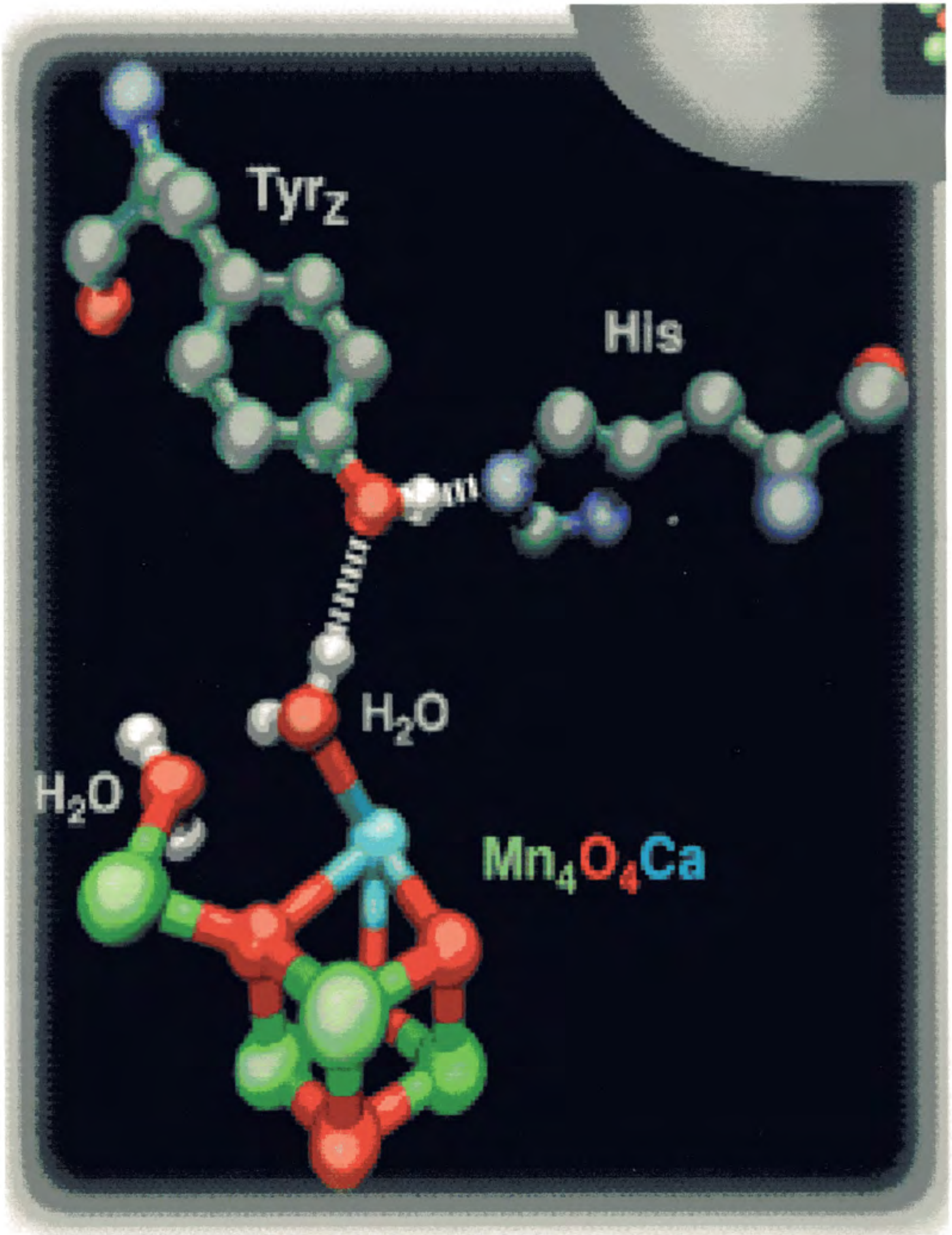






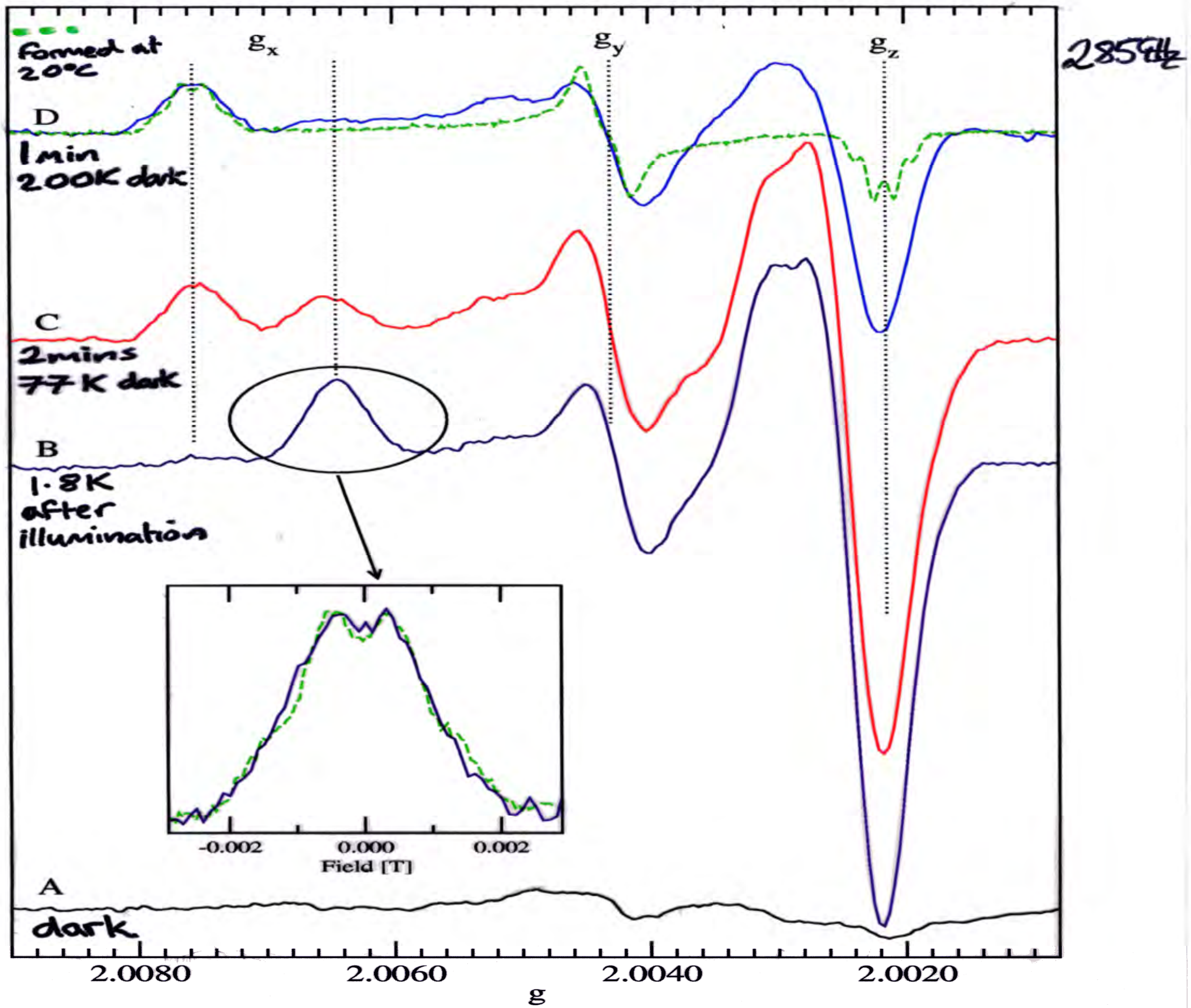






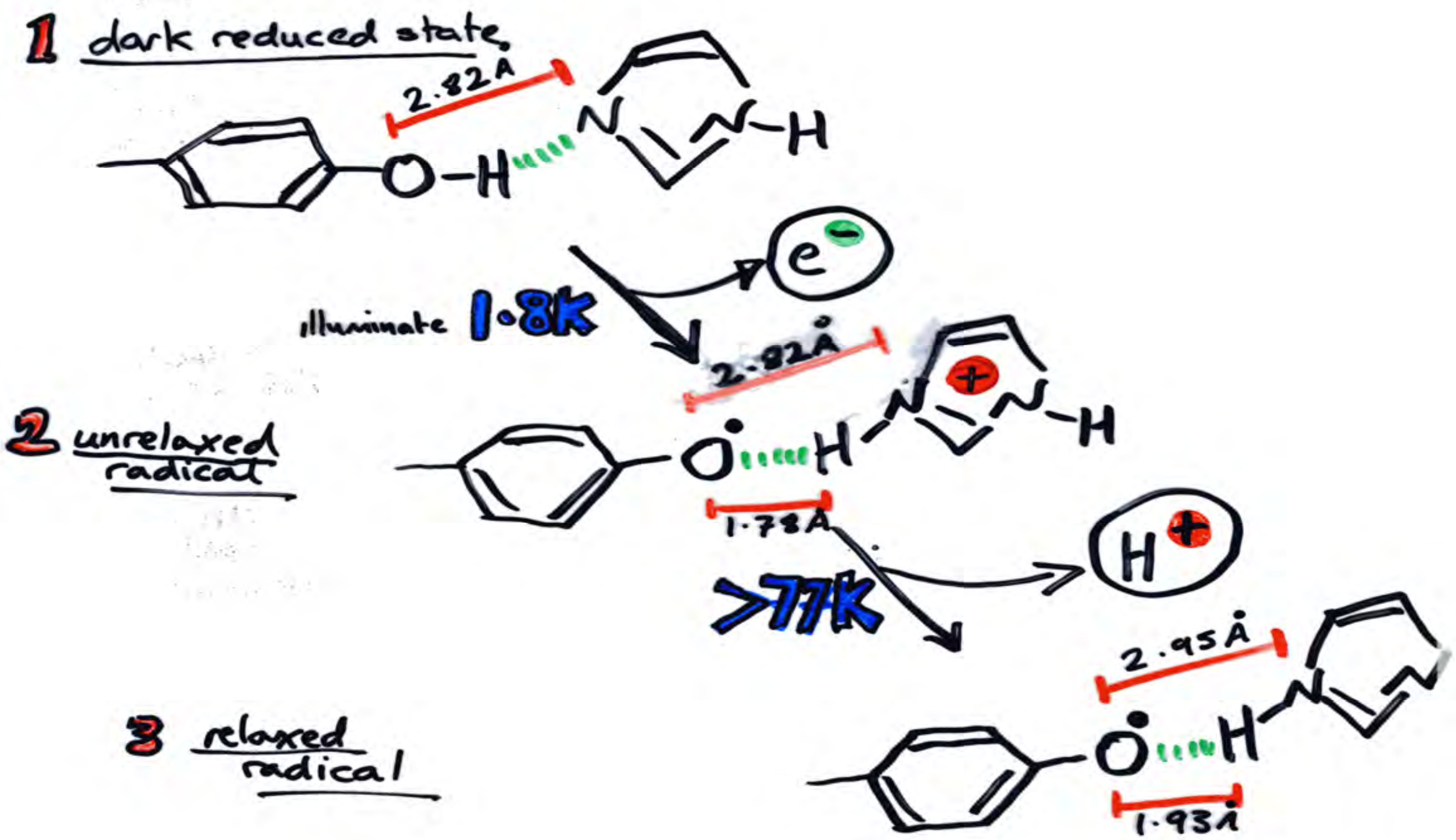
Tyr$_Z$
His
H_2O
H_2O
Mn_4O_4Ca

Tyr D oxidation at cryogenic temperature

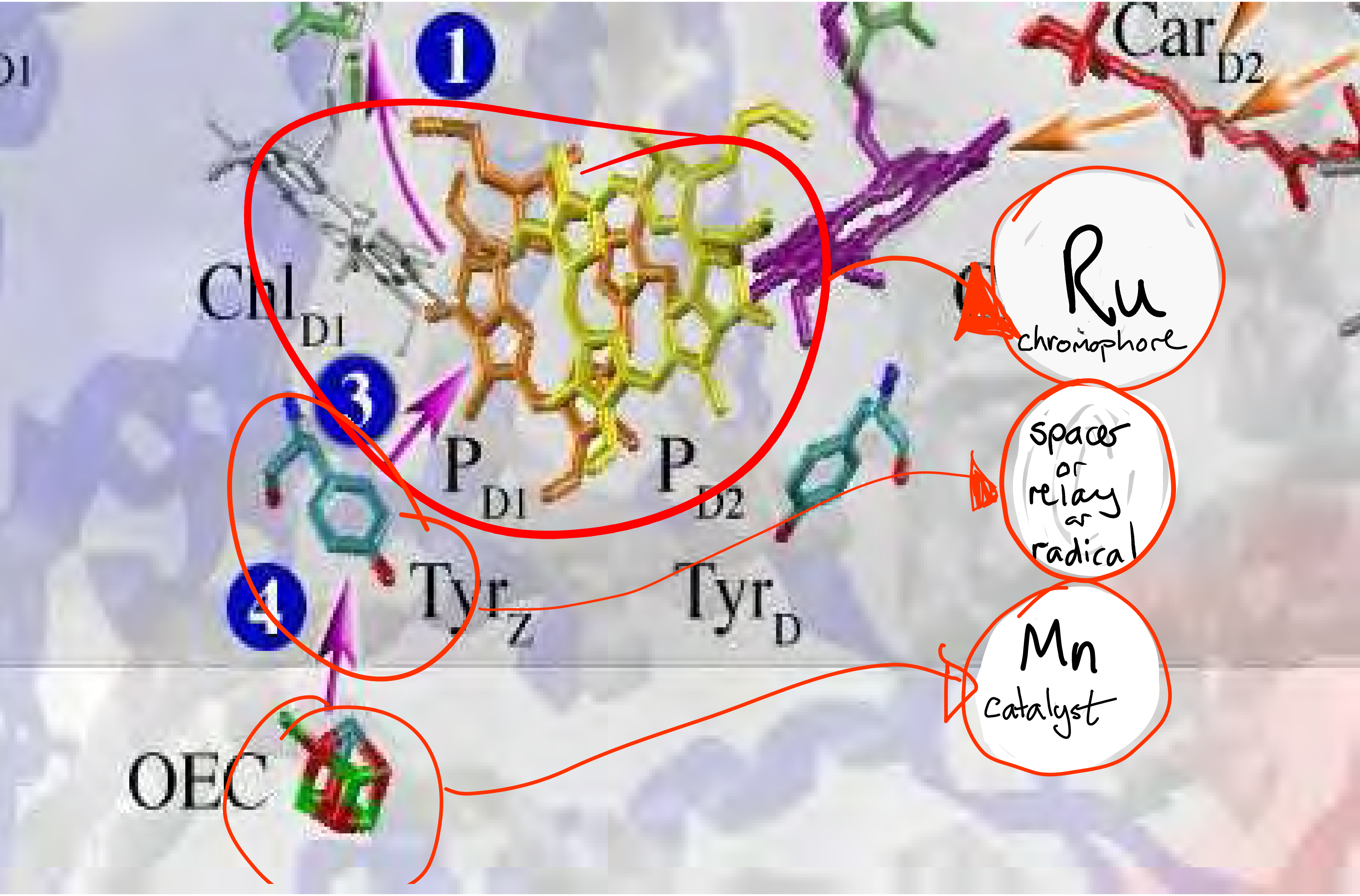


Faller et al 2003

Model a : protontunnelling (pcet)

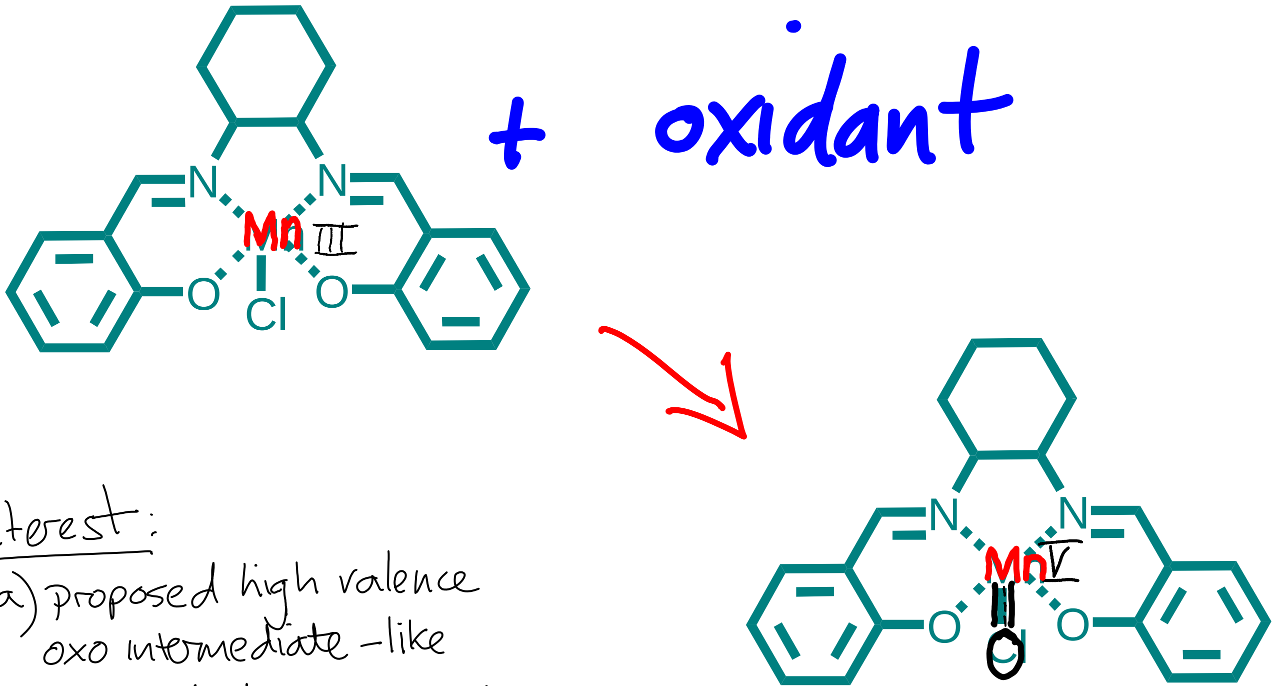


the sequential electrostatic environments track proton movements (or compensation)



Car
D2
1
Chl
D1
3
P
D1
P
D2
4
Tyr
Z
Tyr
D
OEC
Ru
chromophore
spacer
or
relay
or
radical
Mn
catalyst

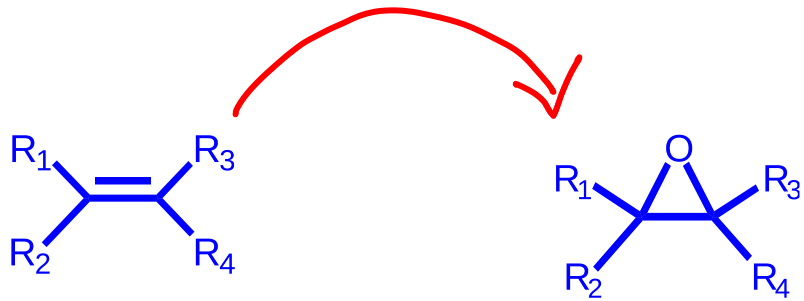
1) The Jacobsen Catalyst



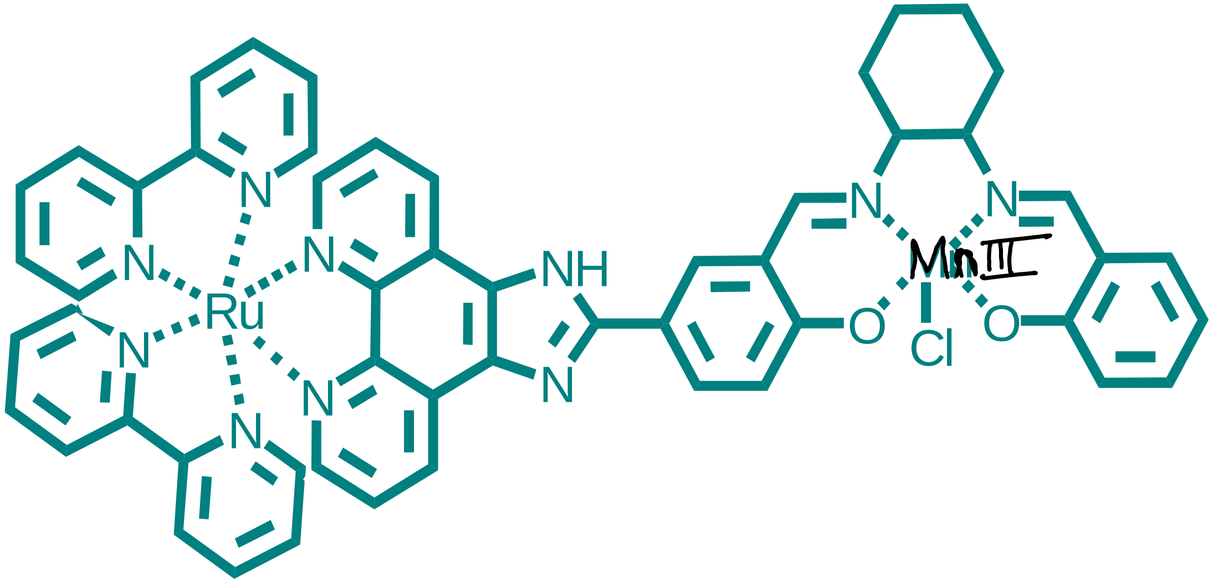
Interest:

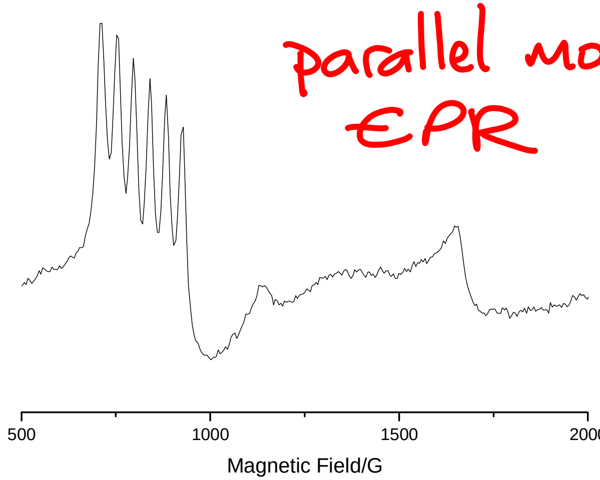
a) proposed high valence oxo intermediate - like water oxidizing enzyme

b) it is a useful catalyst



A photodriven Jacobsen catalyst





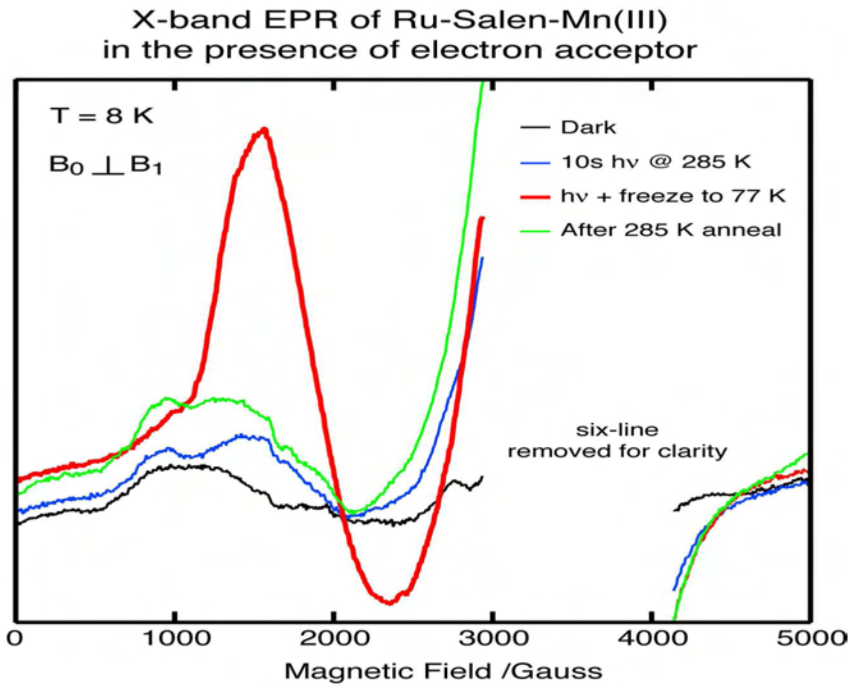
parallel mode EPR

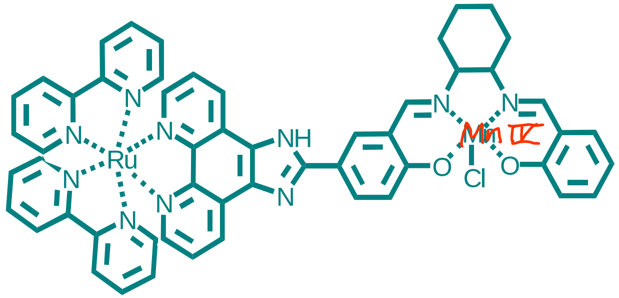
MnIII present and stable

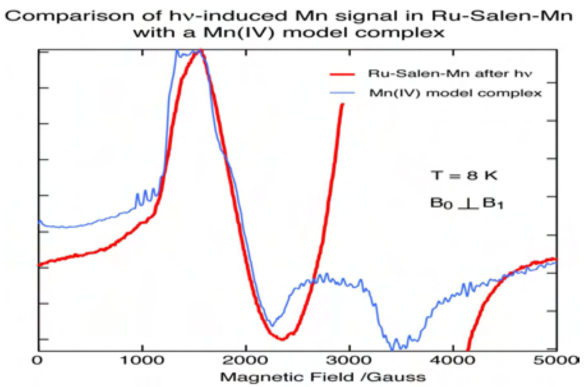
Herrero et al 2008

Freeze in the light + an electron acceptor

Mn goes oxidized





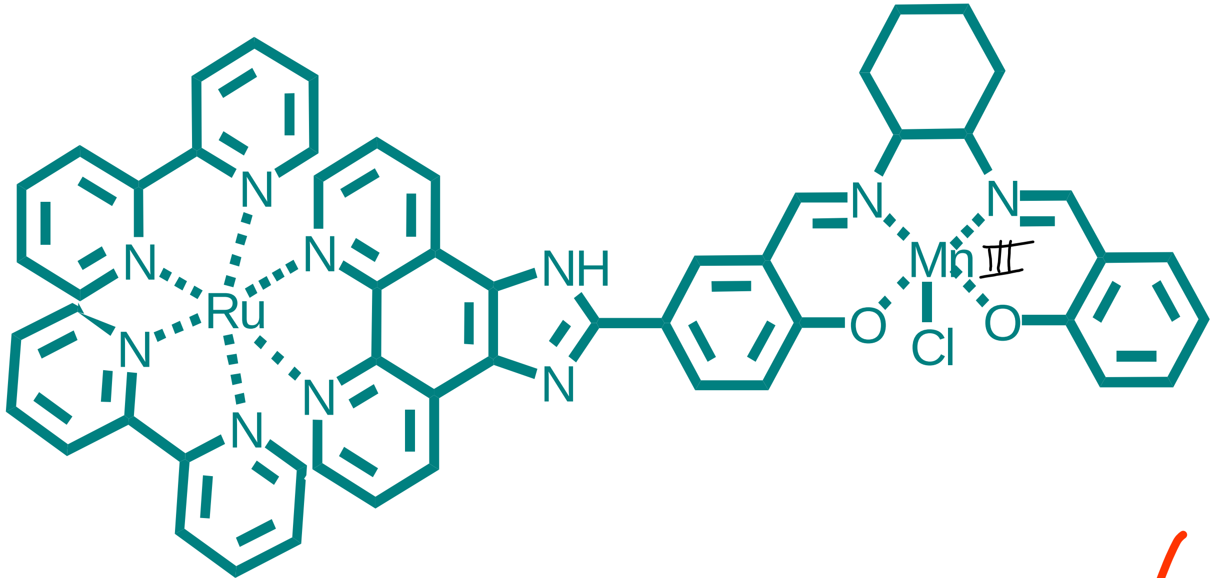


comparison with a Mn IV complex that gives a typical spin 3/2 EPR signal

Herrero et al 2008

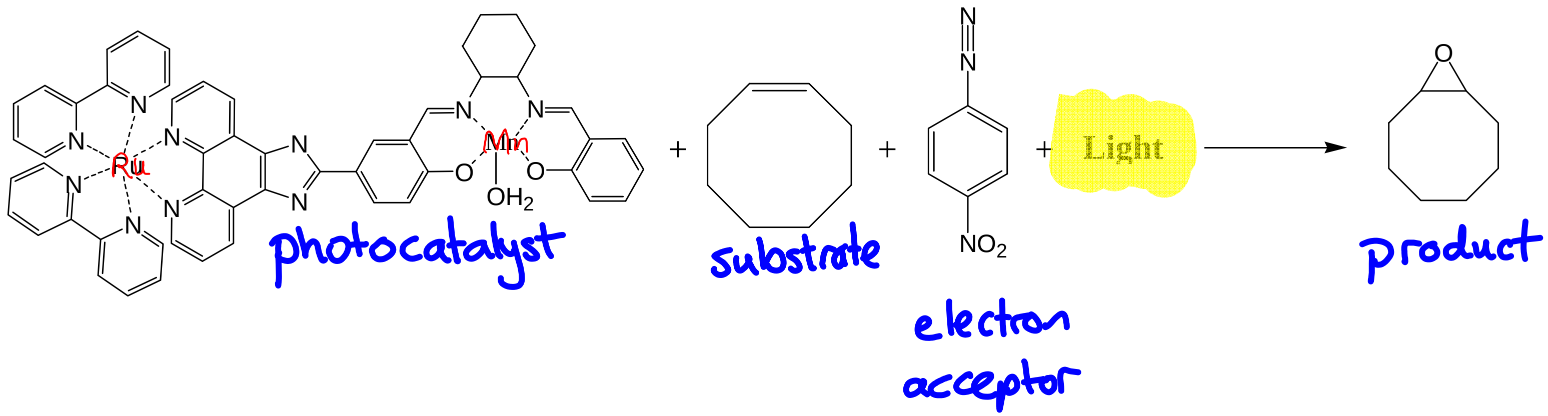
A photodriven Jacobsen catalyst

now add the substrate . . .



switch on the light and it works !

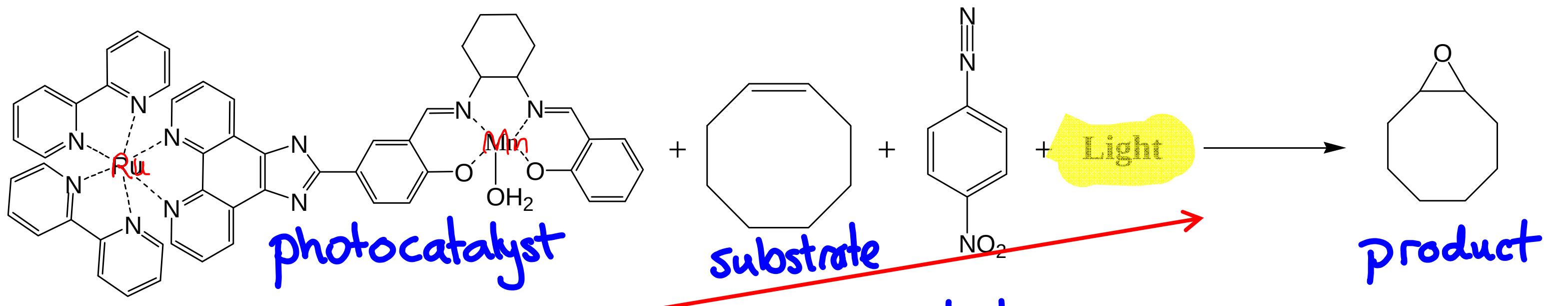
To test for activity, use mass spec.

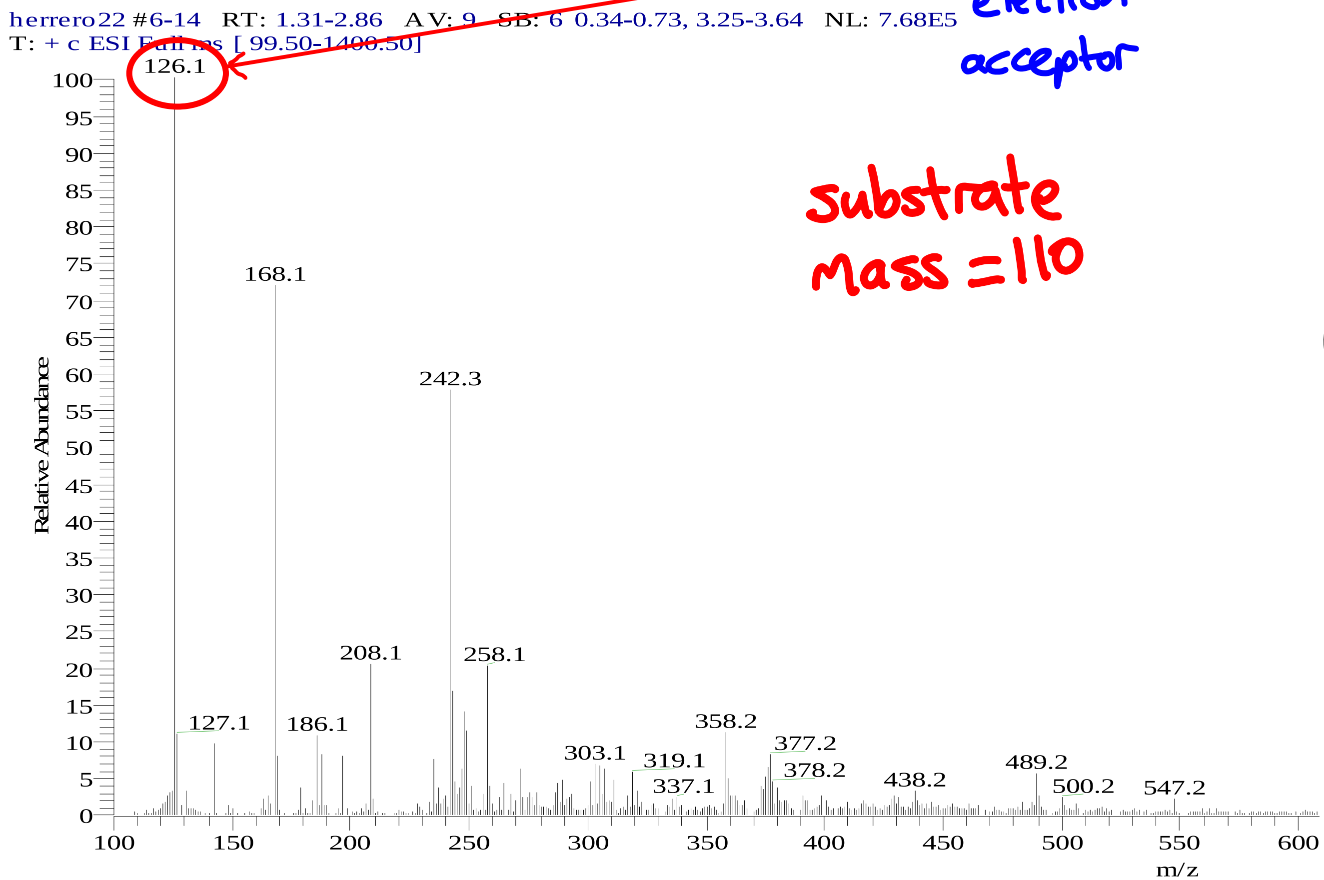


substrate
mass = 110

Herrero et al 2009

To test for activity use mass spec





substrate mass = 110

product mass = 126

(i.e. + one oxygen)

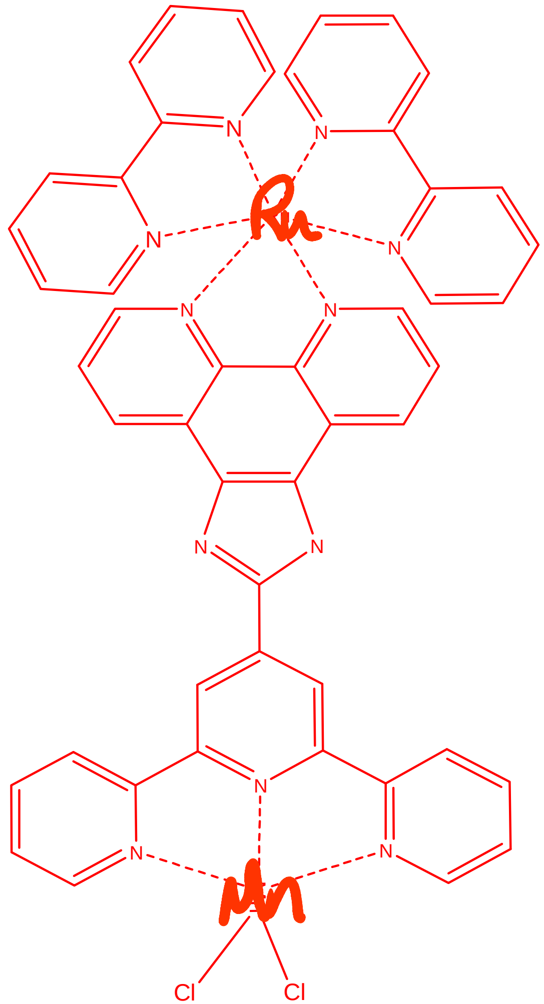
Herrero et al 2009

Another Ru-Mn model

photoactive chromophore –

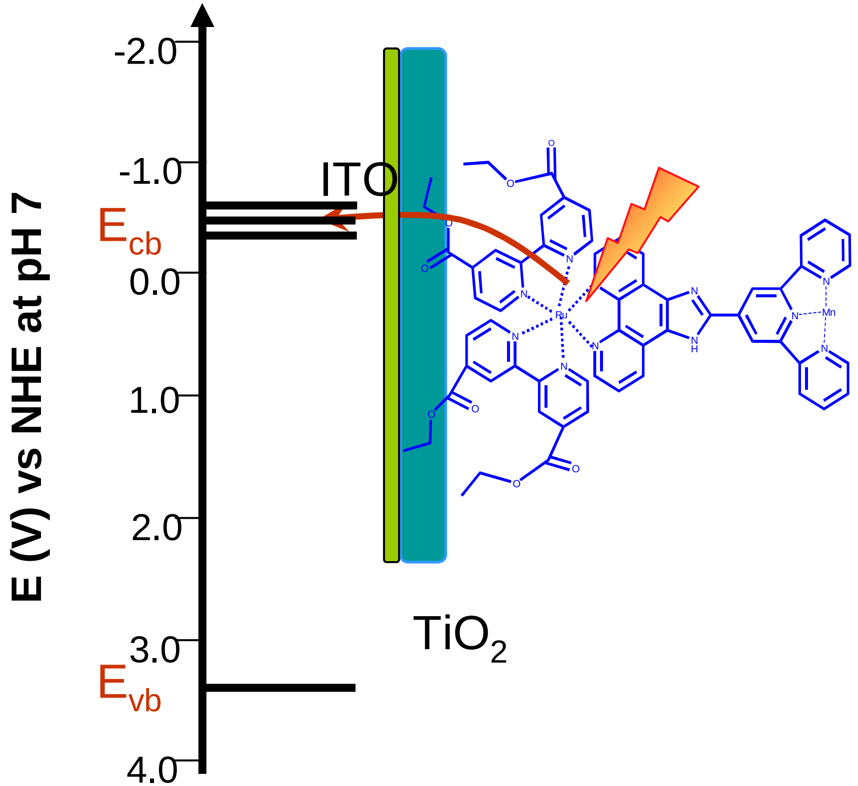
spacer –

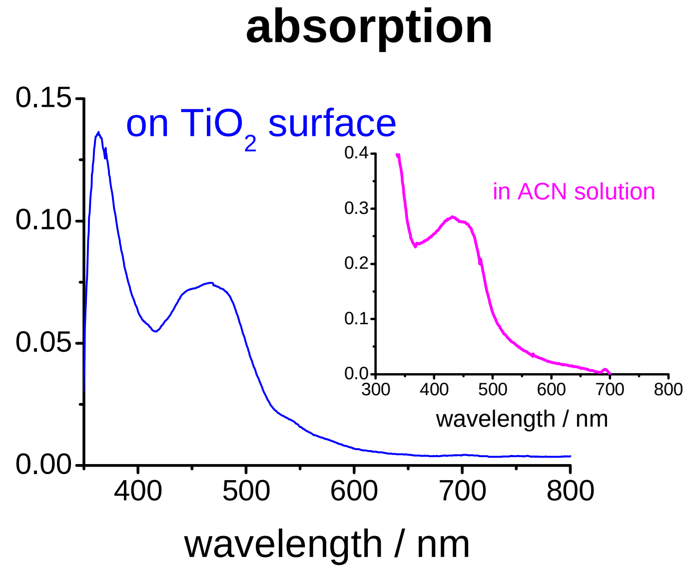
catalytic part –

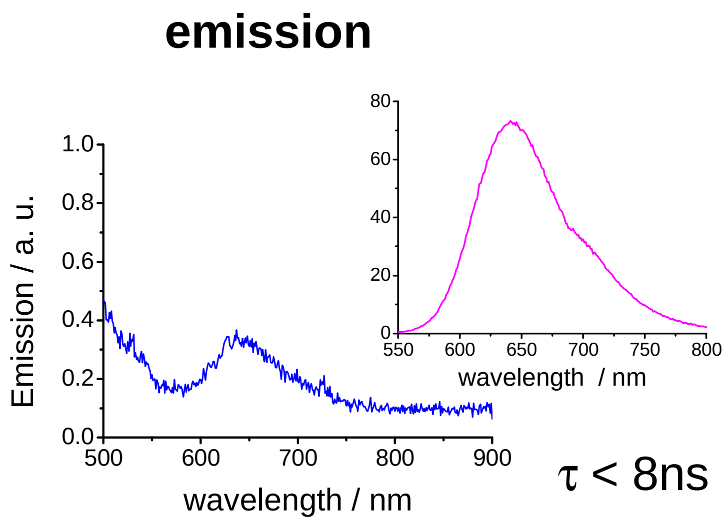


Herrero et al 2008

Grafting on surface







$\tau < 8ns$

➧ *Next: photocurrent measurements*

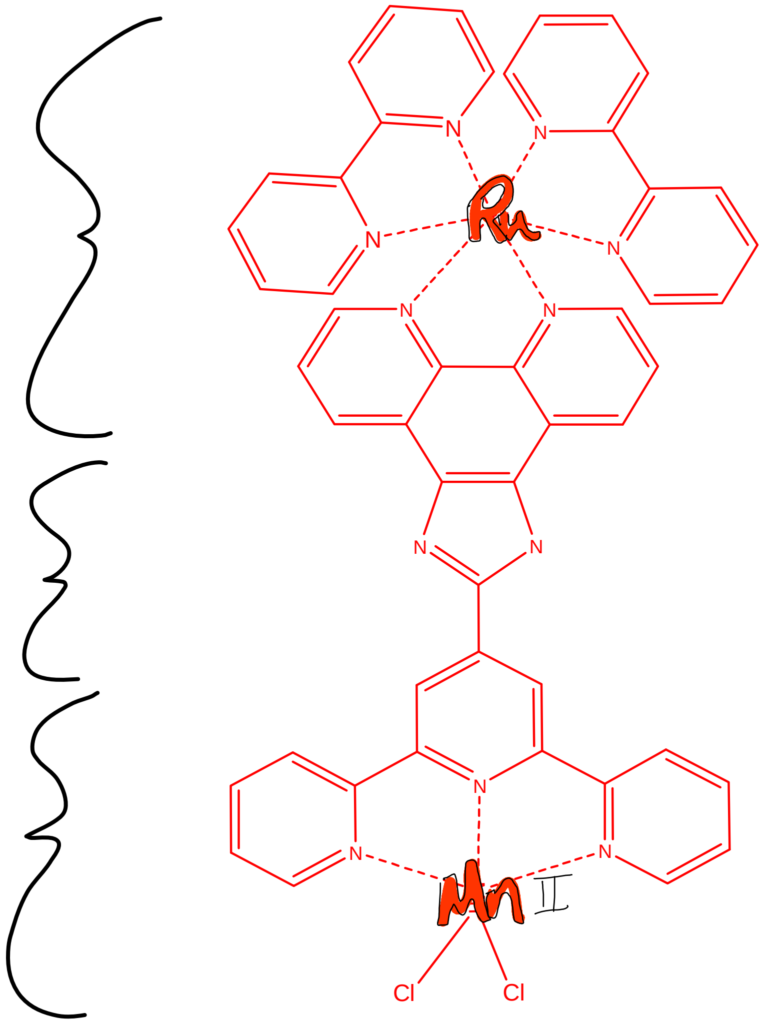
Herrero et al 2008

Another Ru-Mn model

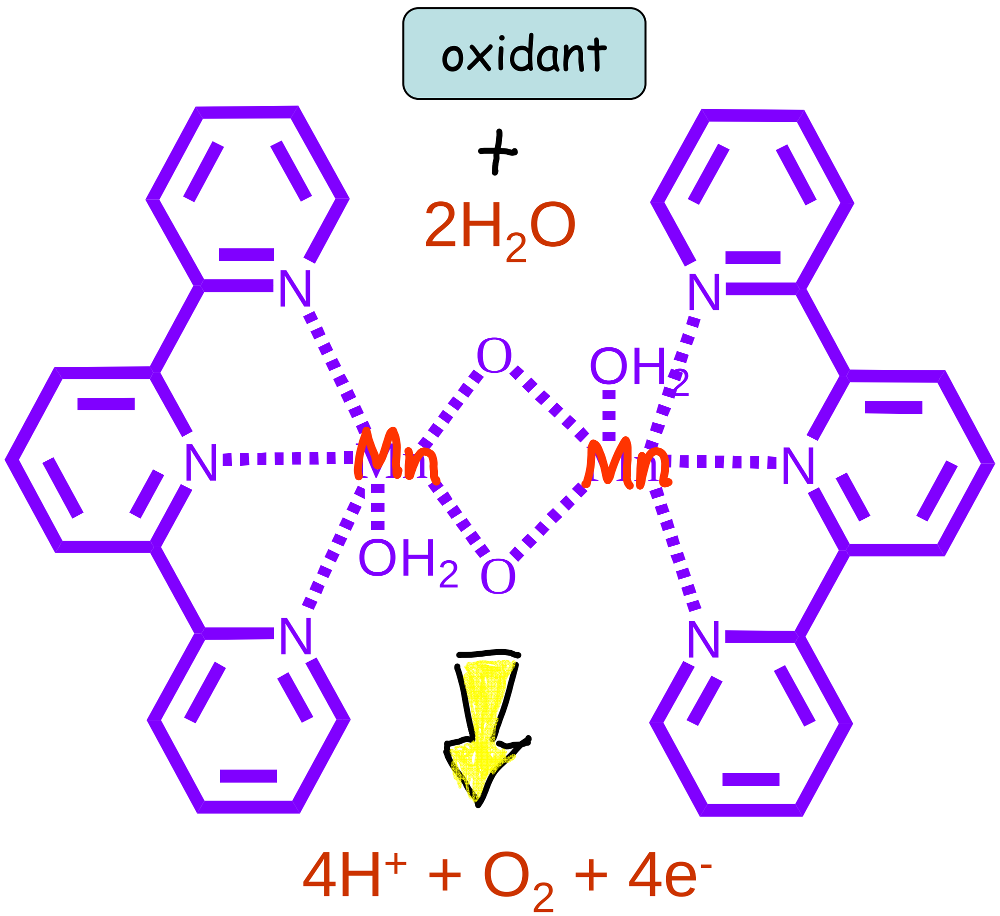
photoactive chromophore —

spacer —

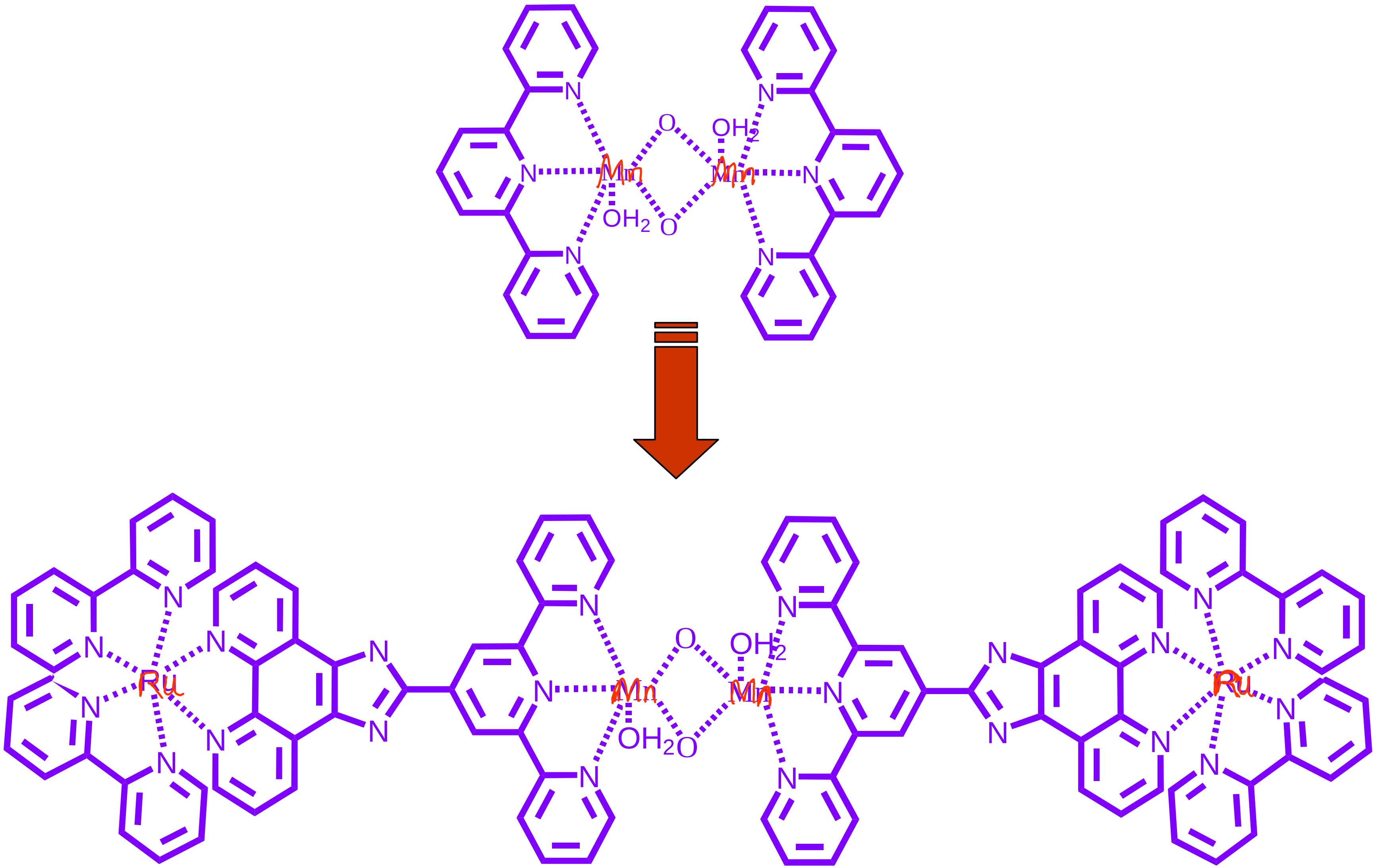
catalytic part —



The "Brudvig" catalyst

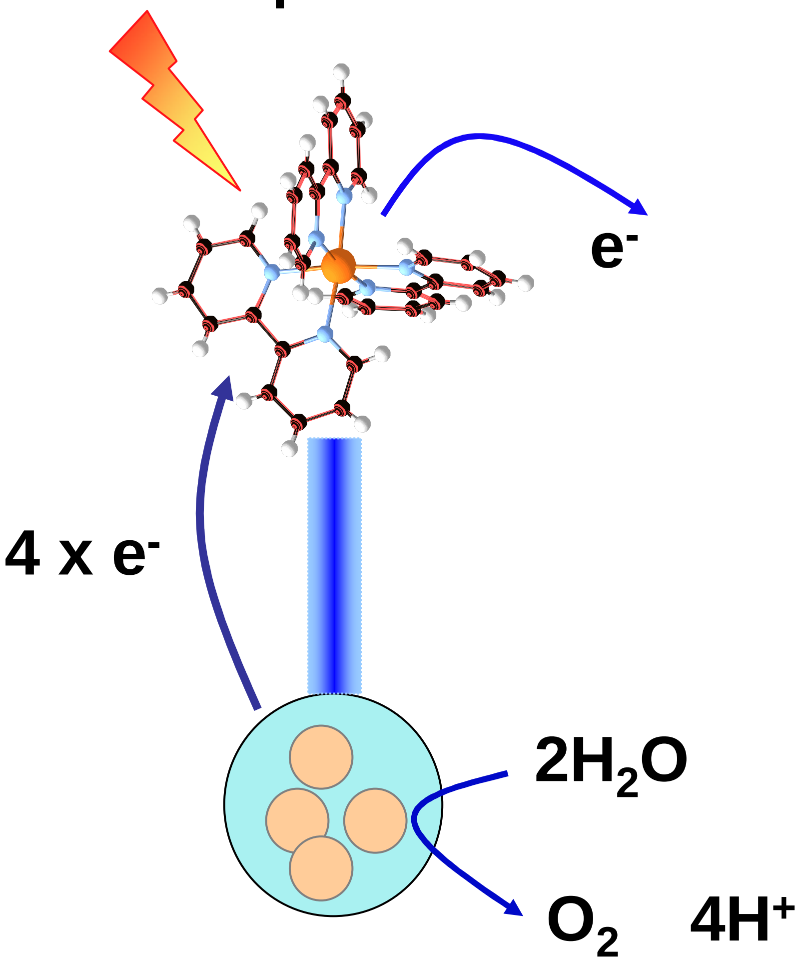


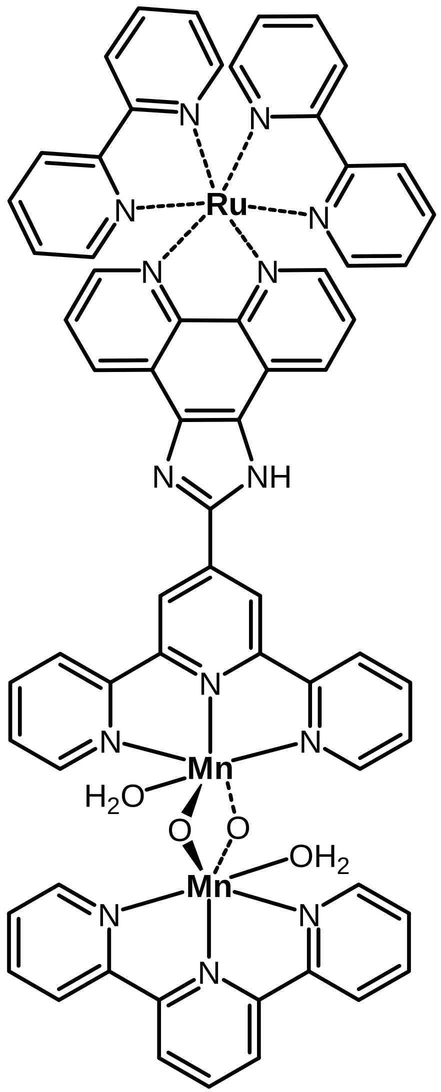
A photo-driven "Brudvig" catalyst



Herrero et al 2008

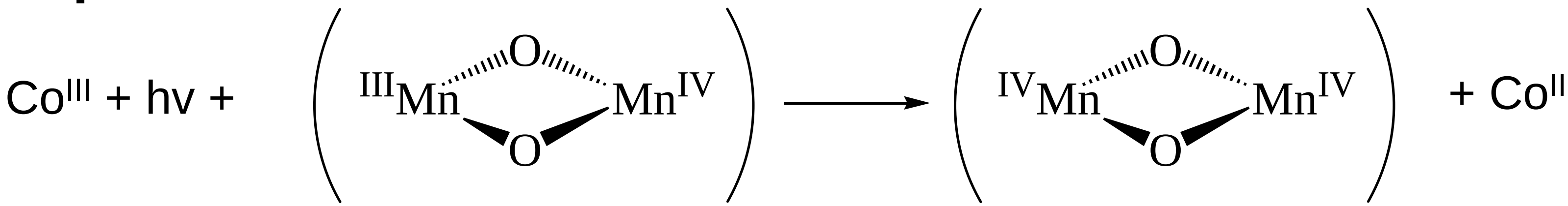
Structure of an Artificial System

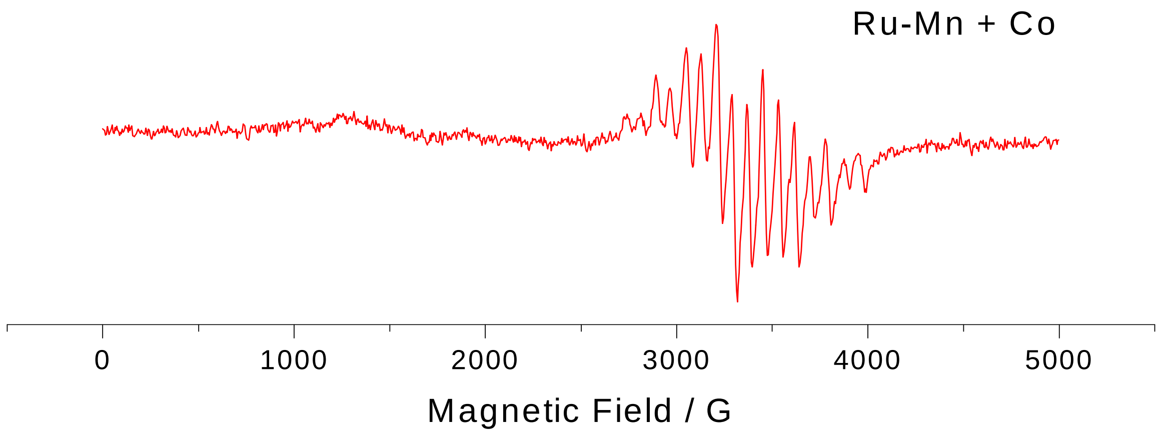


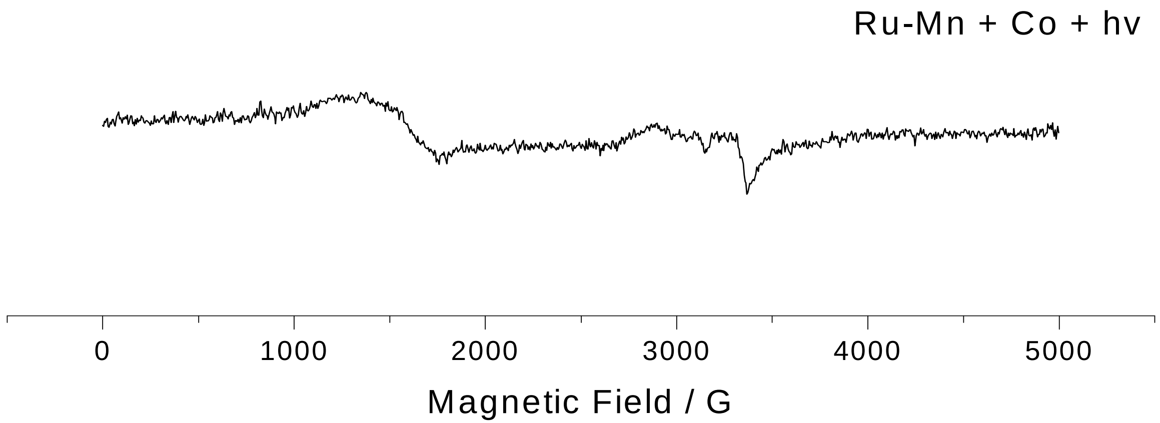


Herrero et al 2008

Light oxidation. Ru Terpyridine Mn_2 di-μ-oxo







Herrero et al 2008

and oxidation

of water?

stay tuned...

Directions

1 Molecular enzymology of PSII

- improved structures
- intermediates
-

2 Artificial systems that work

- linked to surfaces/materials
- multinuclear complexes >2
- photoassembly

Saclay :

UNIVERSITÉ PARIS-SUD 11

ICMMO :

Bioinspired Chemistry
Annamaria Quaranta
Christian Herrero
Vanina Lahootun
Simon Ulmer
Joe Hughes
Winfried Leibl
Ally Aukauloo

Inspired Biochemistry
Naoko Ishida
Arezki Sedoud
Thanh-Lan Lai
Alain Boussac

Fabien Lachaud
Benedikt Lasalle
Marie-France Charlot
Elodie Anxolabéhère-Mallart
Ally Aukauloo

Other Saclay groups
Anja Krieger et al
Sun Un et al
Kirilovsky et al

[1]Laboratoire de Chimie Inorganique, UMR CNRS 8613, Université Paris Sud XI
[2]iBiTec-S, URA CNRS 2096, CEA-Saclay

Chaires internationales de recherche Blaise Pascal

Tom and Ana Moore,
Arizona State University

SOLAR-H

BIOHYDROGÈNE DSV

ANR AGENCE NATIONALE DE LA RECHERCHE

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Ally Aukauloo

Time resolved optical studies on PSII from the IBPC Paris

Fabrice Rappaport

Ehime University
M. Sugiura

Crystallography at Imperial College London

J.Barber
J.Kargul
K. Maghlaoui
J.Murray

[1]Laboratoire de Chimie Inorganique, UMR CNRS 8613, Université Paris Sud XI
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Z Deak
I Vass

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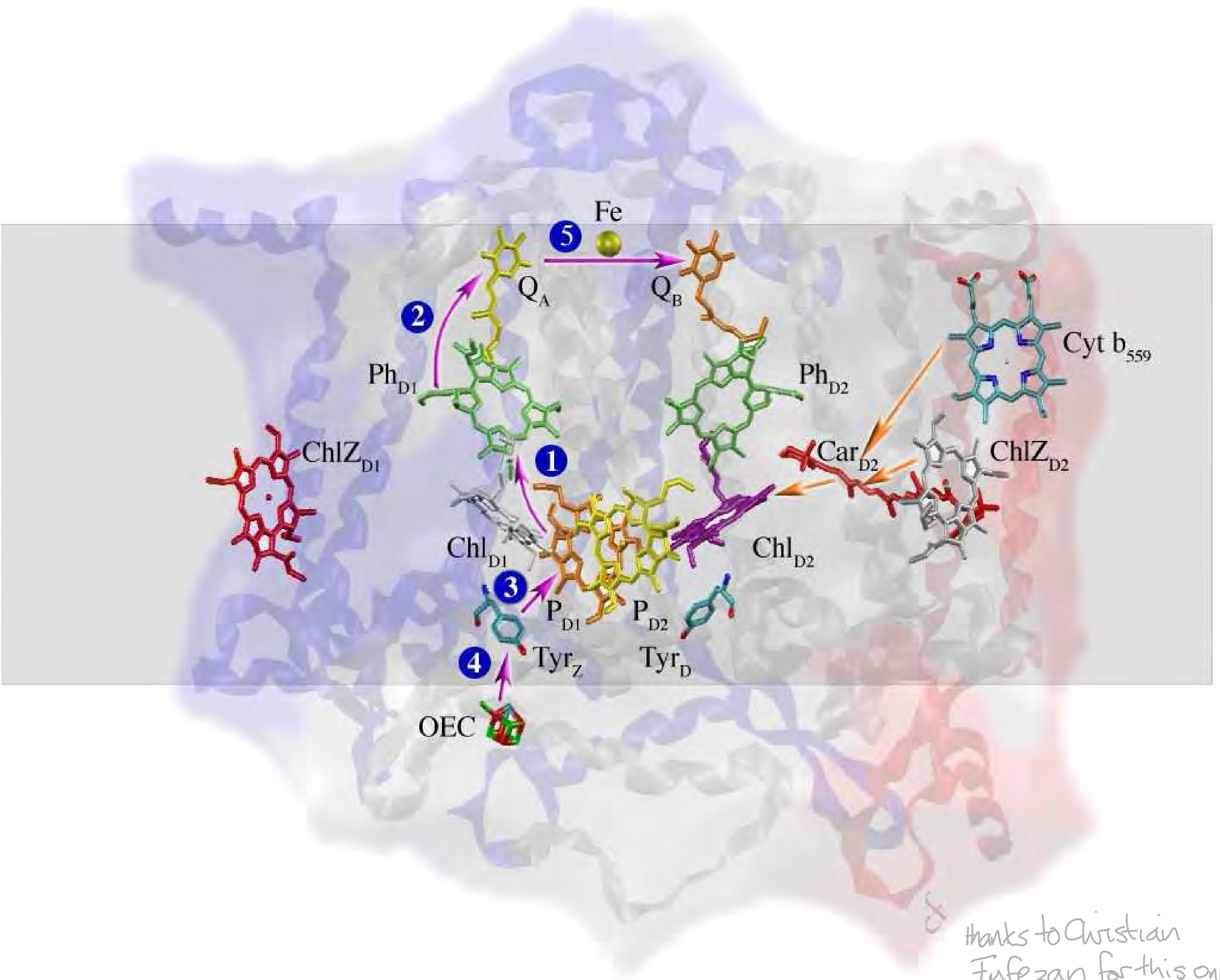
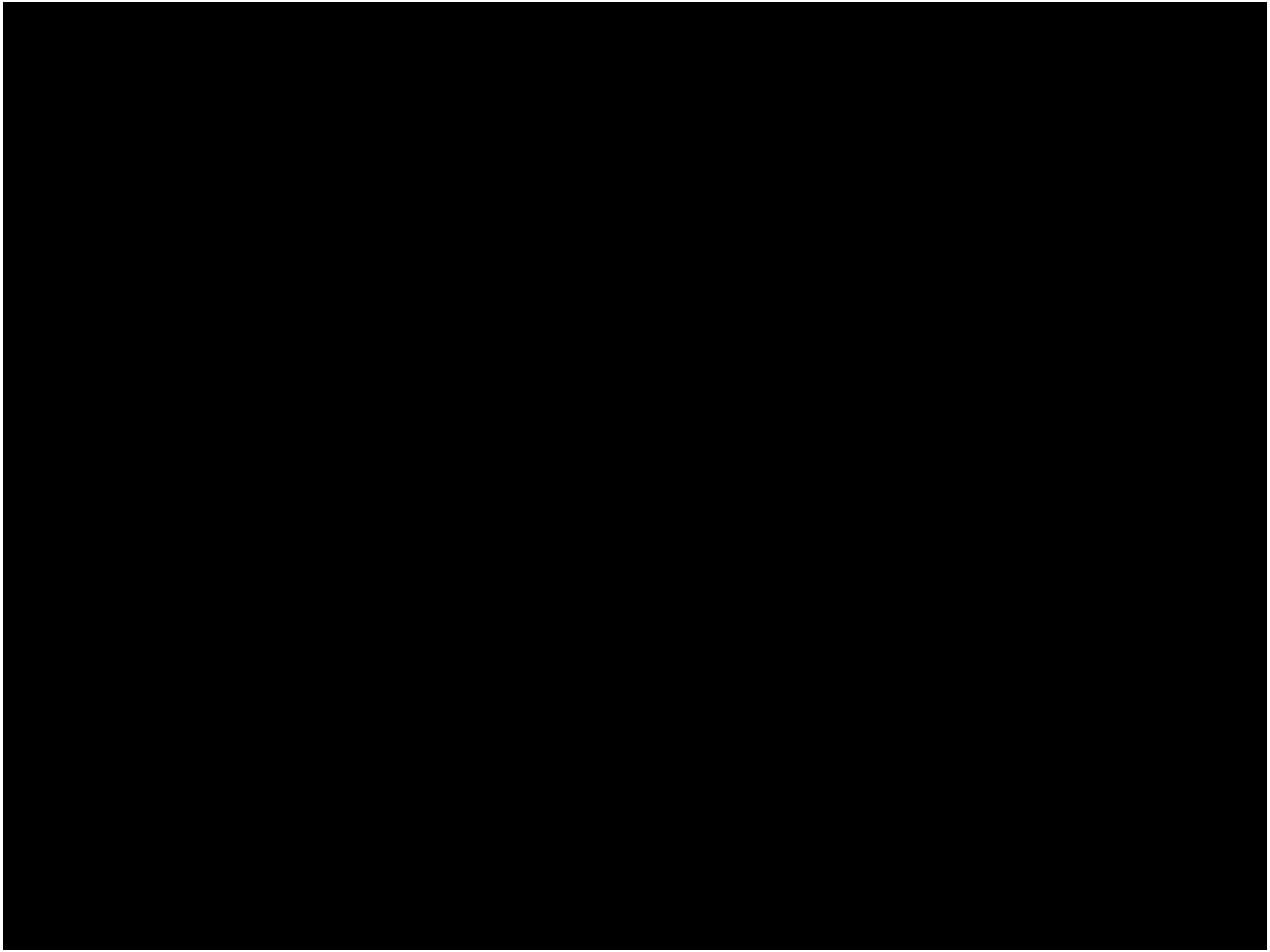


thanks to Christian Fufezan for this one

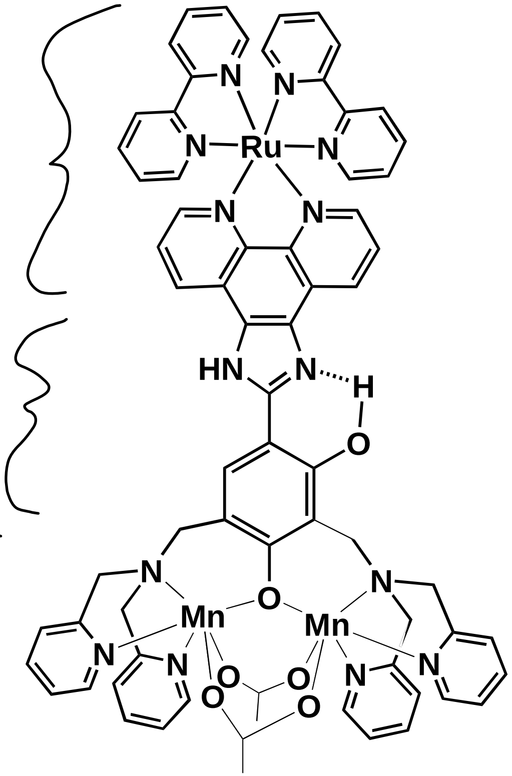


Ru-Mn dimer model with H-bonded phenol radical relay

photoactive chromophore

spacer: H-bonded radical relay

catalytic part



(EPR indicates a Mn dimer)