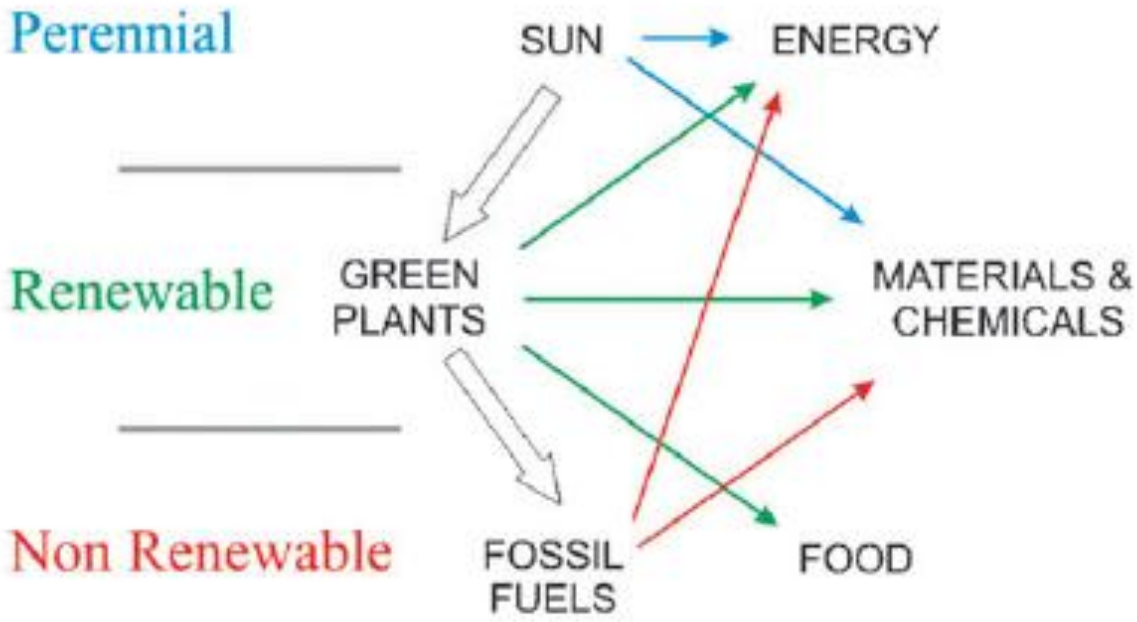
Photocatalysis and sustainability

«…using aggressive reagents and high temperatures is almost unavoidable when carrying out an organic synthesis in the laboratory… plants, give us the marvelous example of great results obtained by usign minimal means…. One should first consider enzymes… there is another agent of the highest important for plants which deservs to be studied in detail, and this is light.»

G. Ciamician

Solar irradiation: 25000 – 75000 kWh per day and hectar



Photocatalysis and sustainability

To be considered green, a reaction must ensure:

- ✓ **Efficient use of energy sources;**
- ✓ **Minimization of hazards related to the use of chemicals and the reaction conditions;**
- ✓ **Minimization of waste;**
- ✓ **Use of renewable sources.**

Features of photochemical reactions:

- ✓ **Photons as reagents;**
- ✓ **Highly reactive intermediates are obtained under mild conditions;**
- ✓ **High selectivity, low E values;**
- ✓ **Low energy barriers;**
- ✓ **Versatility in the choice of reaction conditions.**

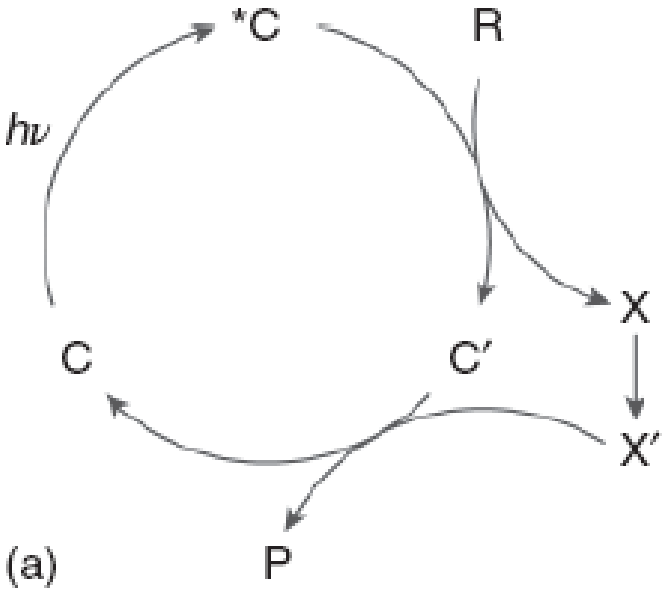
Limitations of photochemical reactions:

- ✓ **Diluted solutions;**
- ✓ **The light source: Solar Light *vs* Artificial sources of Visible Light.**

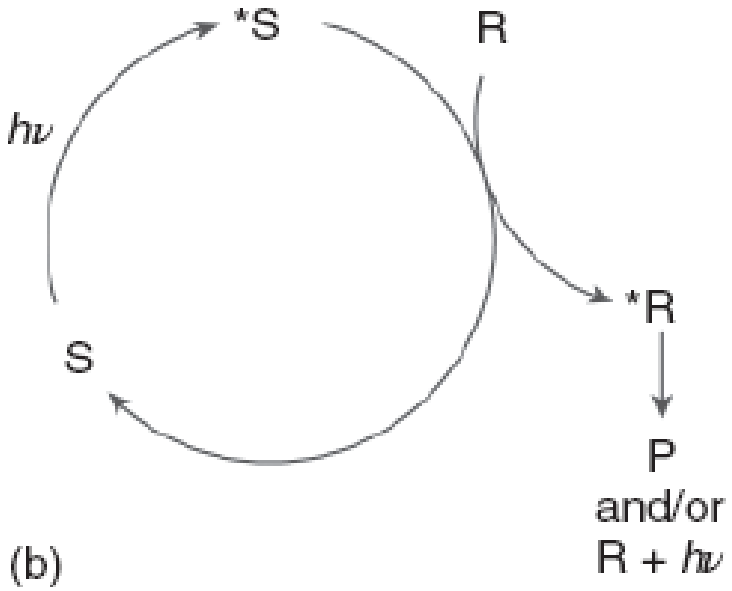
Photocatalysis

Photocatalysis refers to any reaction that requires the simultaneous presence of a catalyst and light.

Photocatalysis



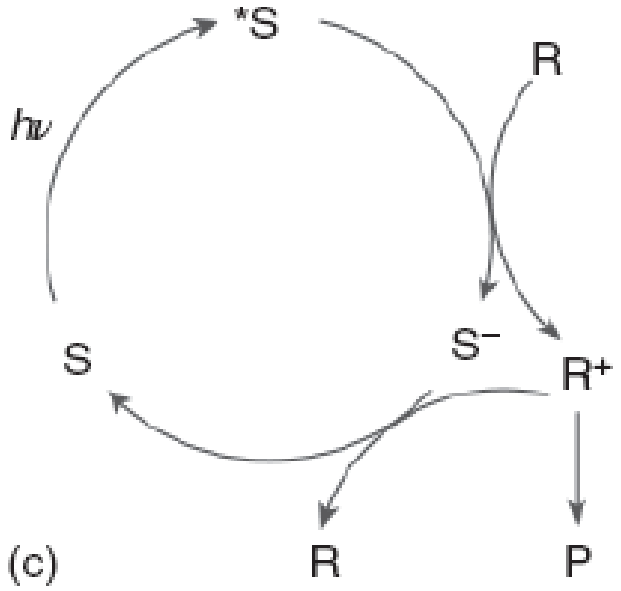
Energy-transfer photosensitization



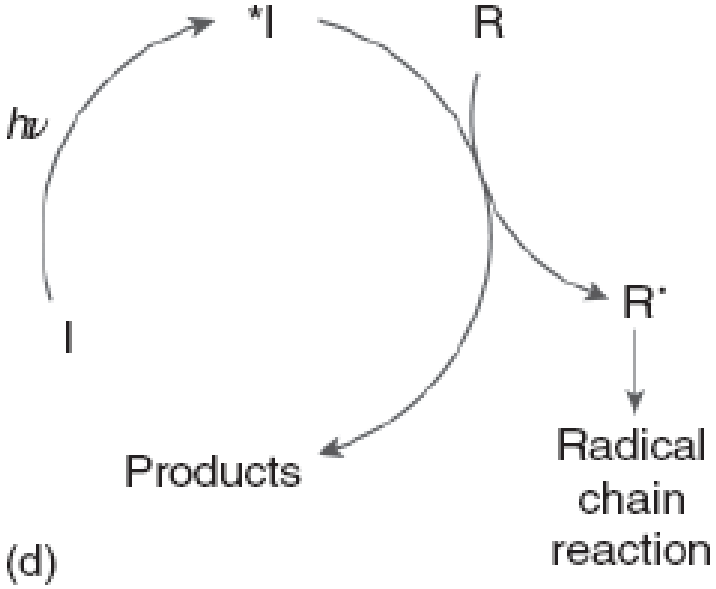
Photocatalysis

Photocatalysis refers to any reaction that requires the simultaneous presence of a catalyst and light.

Electron-transfer photosensitization

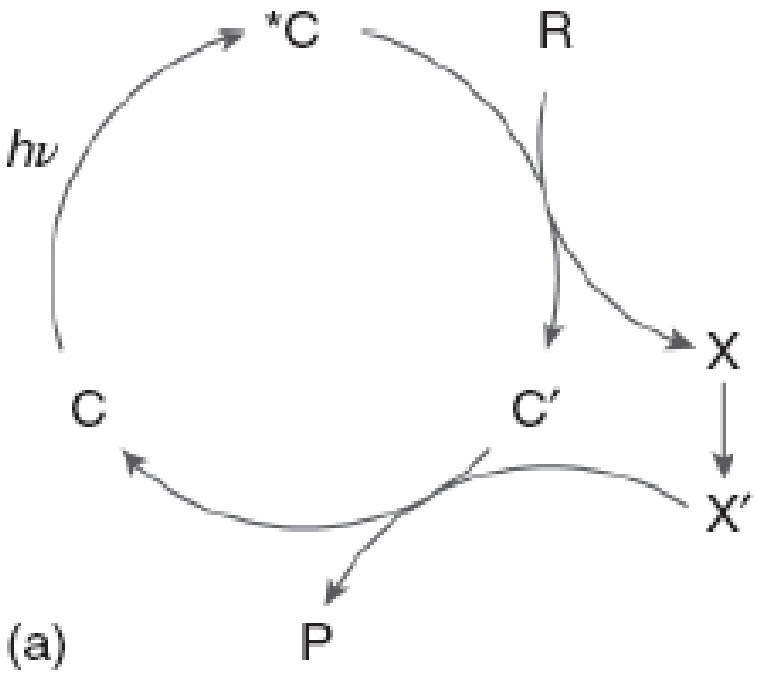


Photoinduced chain reaction



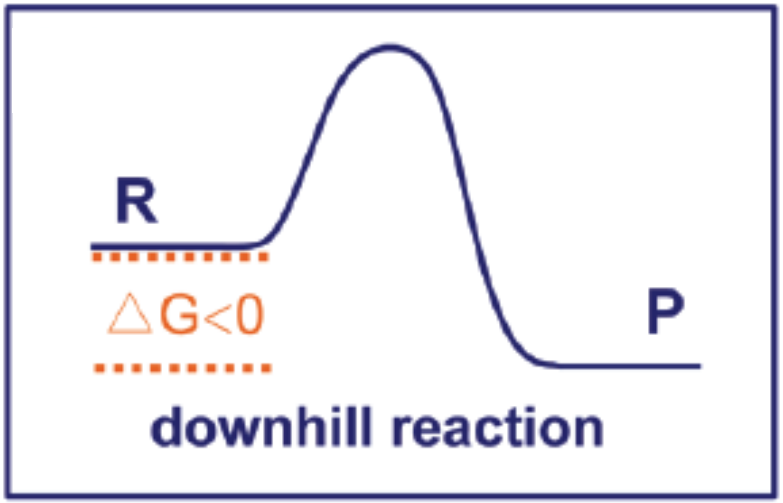
Photocatalysis

Photocatalysis refers to any reaction that requires the simultaneous presence of a catalyst and light.

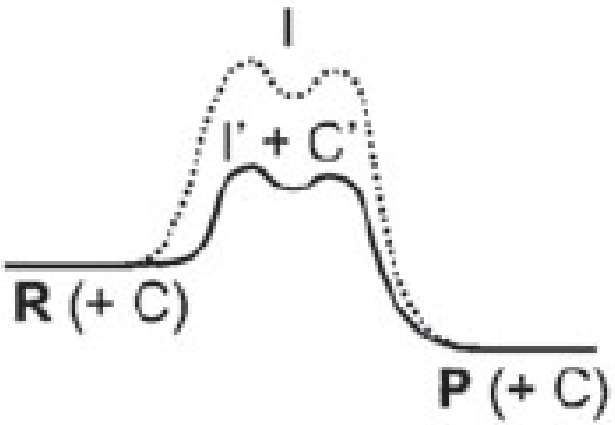


Photocatalysis: Thermodynamic aspects

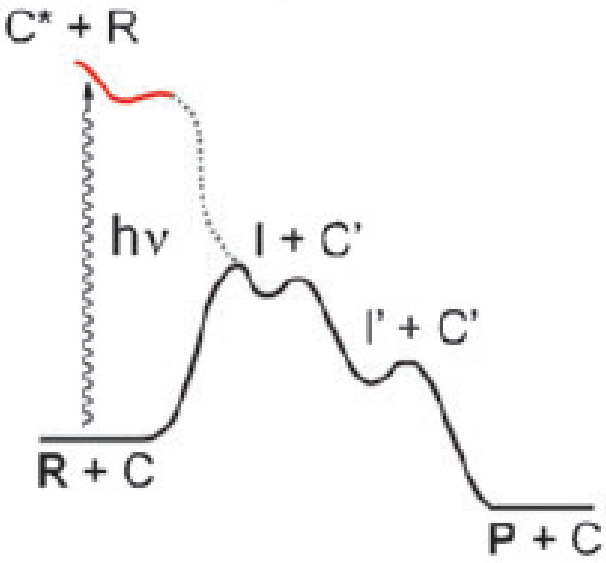
Spontaneous reactions



Thermal reaction

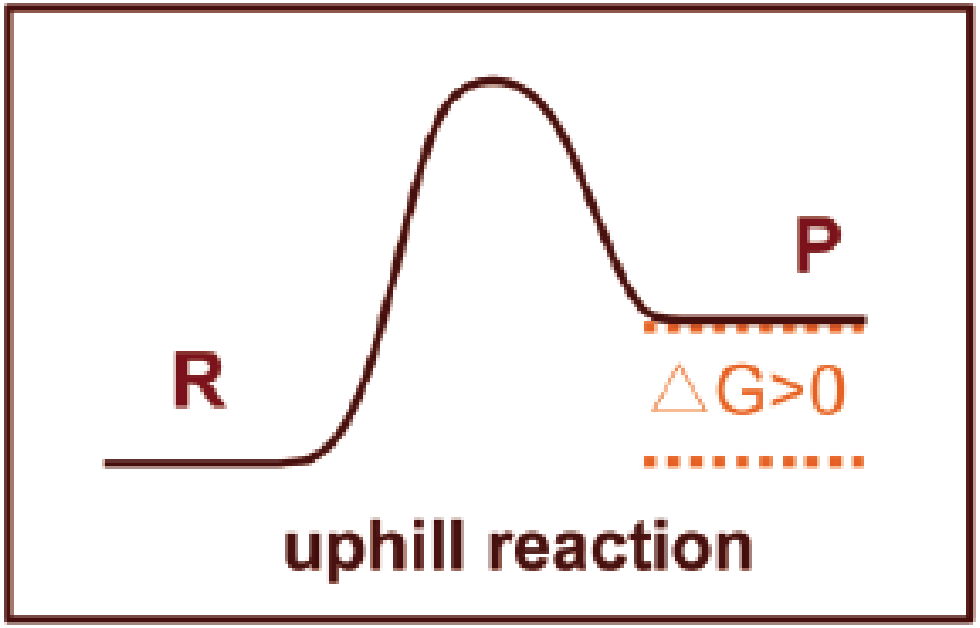


Photochemical reaction



Photocatalysis: Thermodynamic aspects

Non-Spontaneous reactions

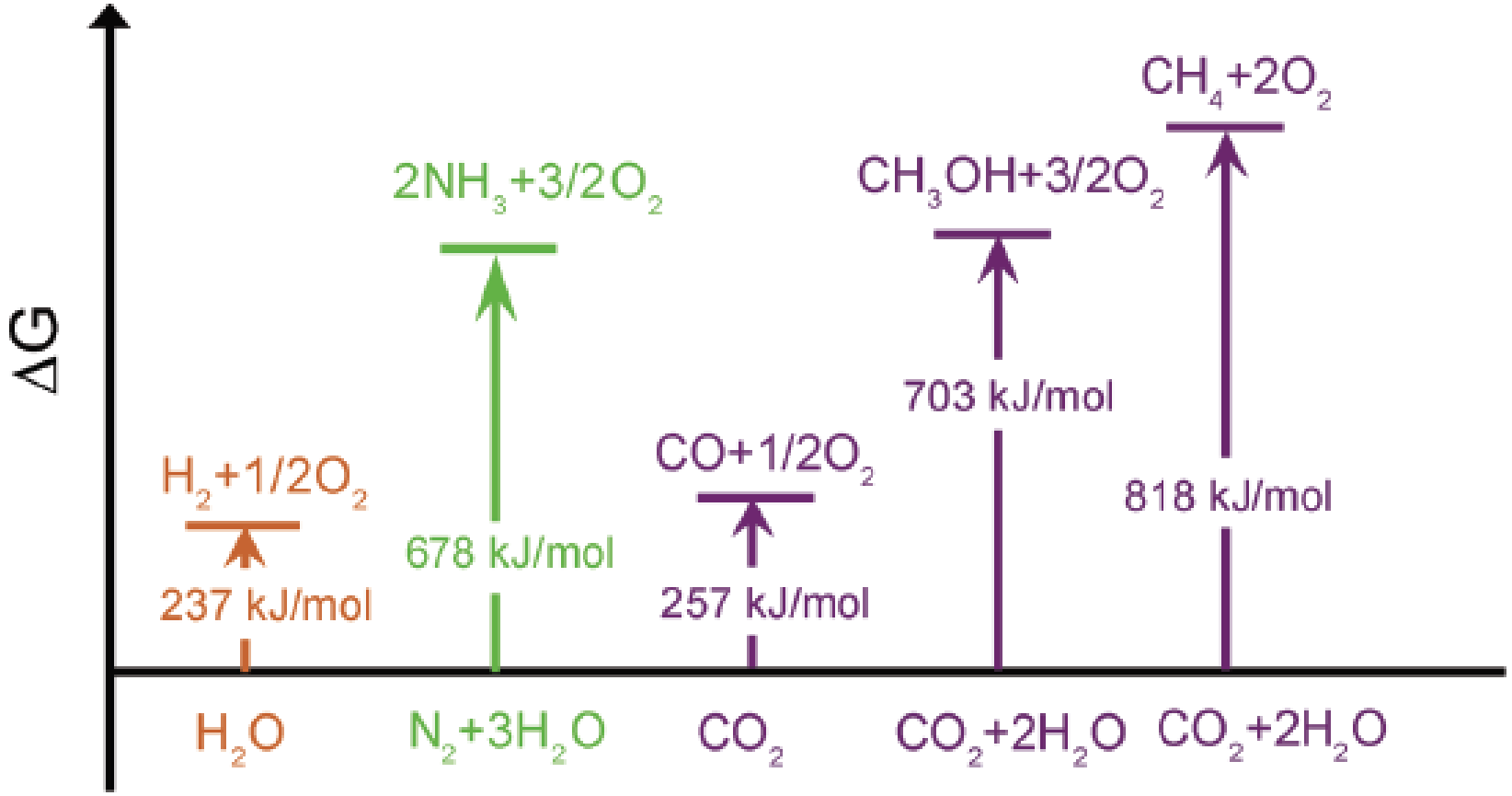


Broader approach

«.. To enhance the power of chemical synthesis by removing current thermodynamic restrictions, I strongly recommend …. to develop a «photosynthetic» catalyst that facilitates a thermally unachievable, energetically uphill reaction.»

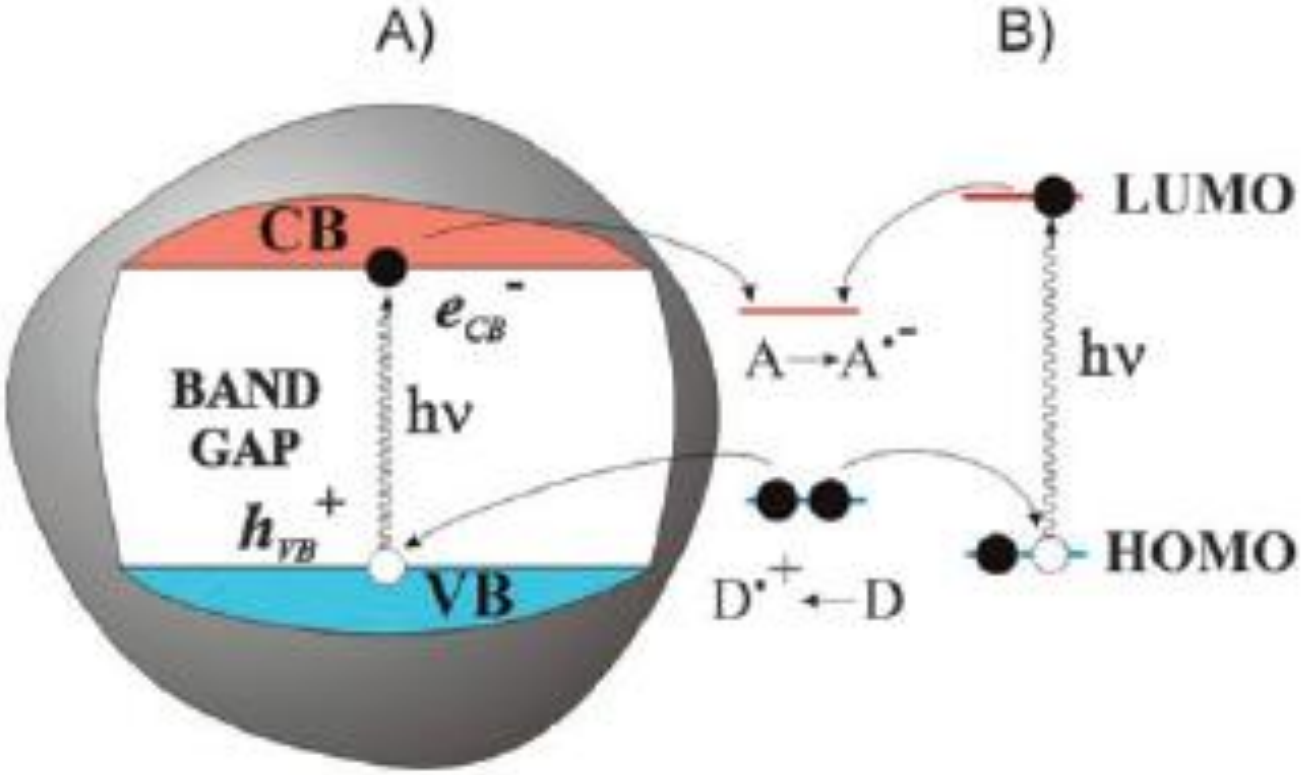
R. Noyori *Tetrahedron* 2010, *66*, 1028.

Thermodynamically uphill reactions



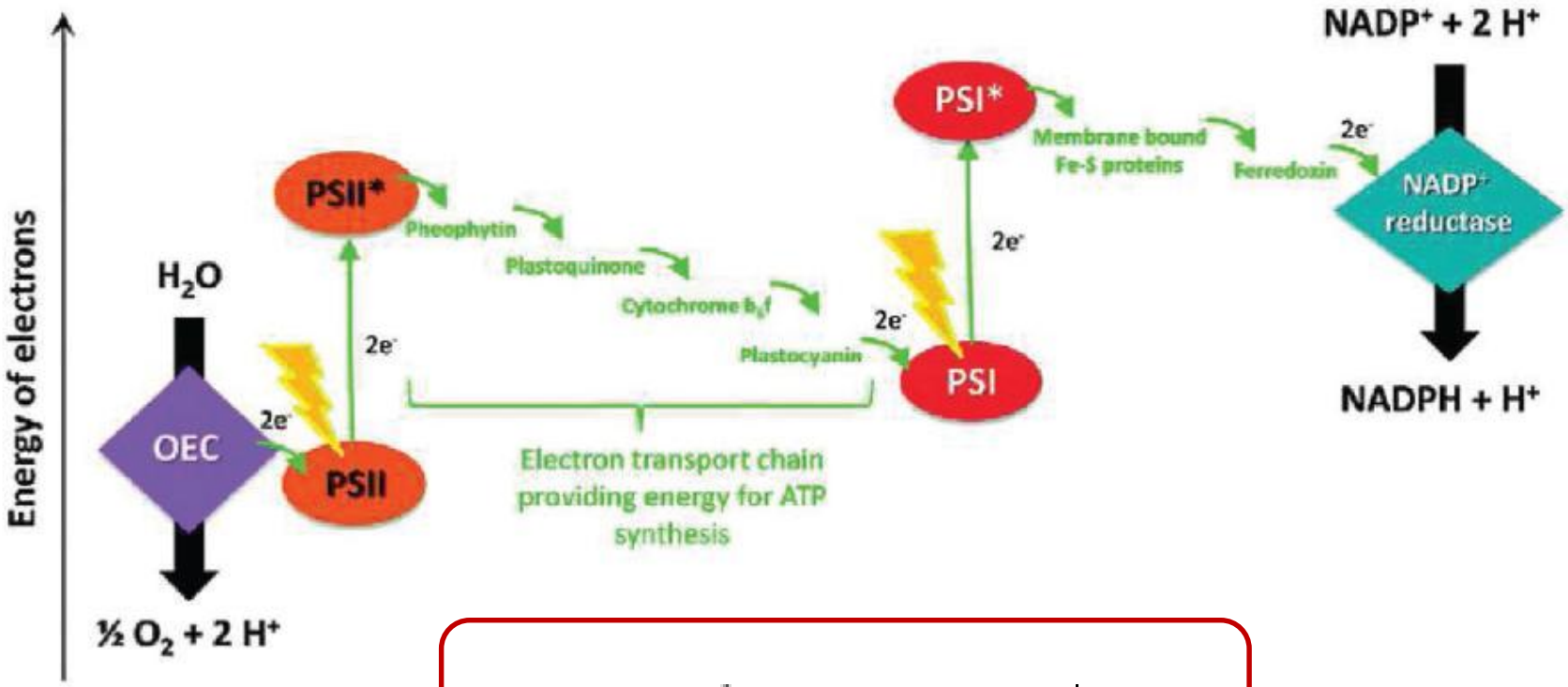
Photocatalysis at semiconductor particles or molecules

Heterogeneous photocatalysis *vs* homogeneous photocatalysis



TON **TOF** **Φ**

Photosynthesis in nature



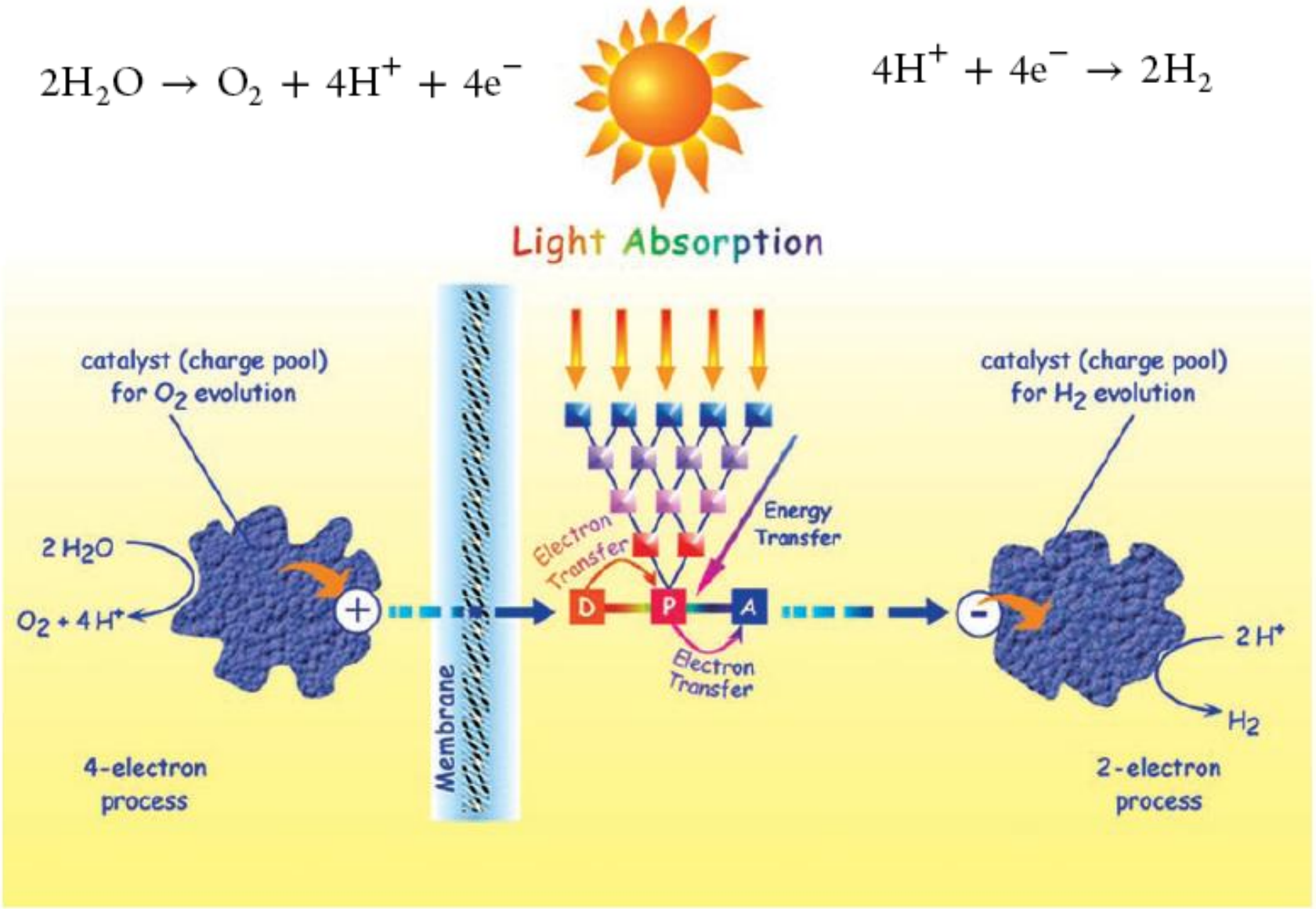
$$2H_2O + 4h\nu \rightarrow O_2 + 4H^+ + 4e^-$$

$$2NADP^+ + 2H^+ + 4e^- + 4h\nu \rightarrow 2NADPH$$

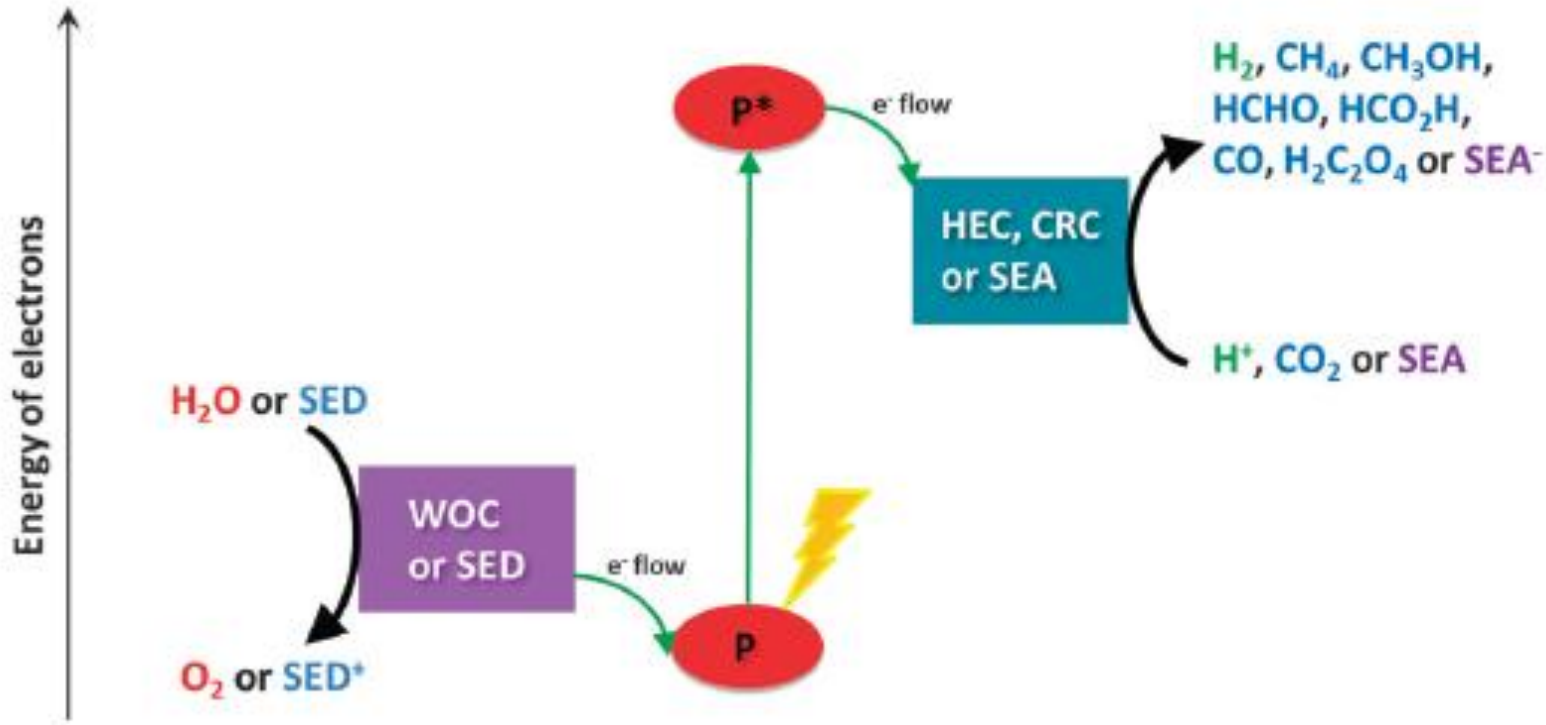
Artificial Photosynthesis

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

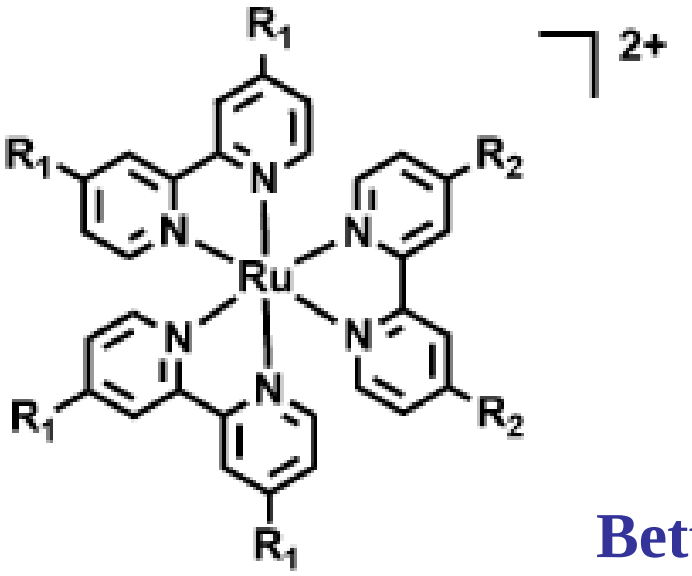
$$4H^+ + 4e^- \rightarrow 2H_2$$



Artificial Photosynthesis

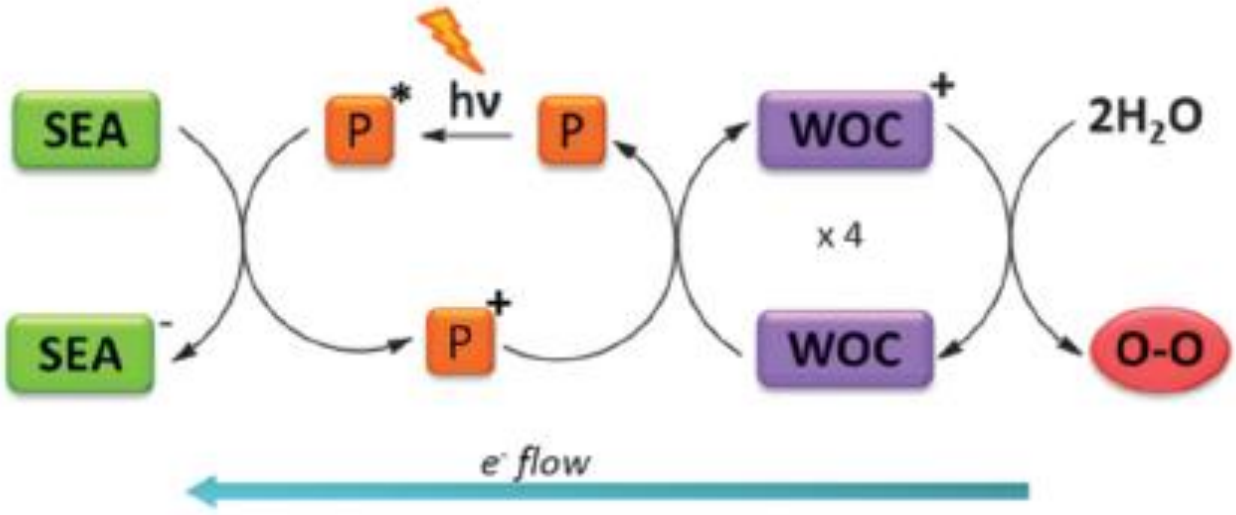


Photosensitizer



- Absorption at 452 nm (visible light)
- Stable, long-lived excited state (τ = 1100 ns)
- Single electron transfer (SET) catalyst
- Effective excited state oxidant and reductant

Better electron donor & better electron acceptor for 2.12 V.



Water oxidation catalysis

$$2H_2O \rightarrow O_2 + 4e^- + 4H^+ \qquad E^0 = +0.82\ V$$

SEA più utilizzati

CAN

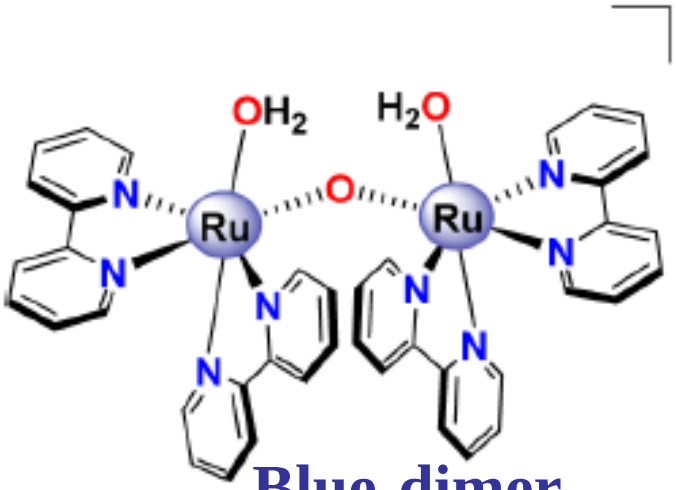
$4Ce^{4+} + 4e^- \rightarrow 4Ce^{3+}$ $\quad E^0 = 1.72$ V

$2IO_4^- + 4e^- + 4H^+ \rightarrow 2\,IO_3^- + 2H_2O$ $\quad E^0 = 1.60$ V

$4[Ru(bpy)_3]^{3+} + 4e^- \rightarrow 4[Ru(bpy)_3]^{2+}$ $\quad E^0 = 1.24$ V

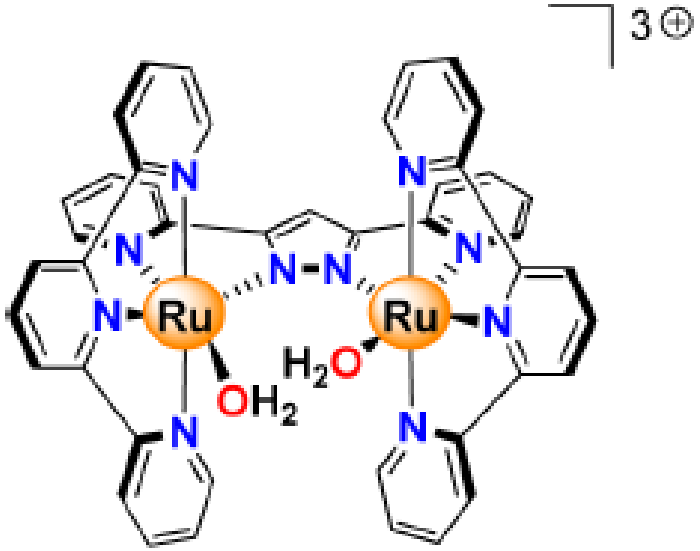
$$2H_2O + n\mathrm{Ox} \rightarrow 4H^+ + O_2 + n\mathrm{Red}$$

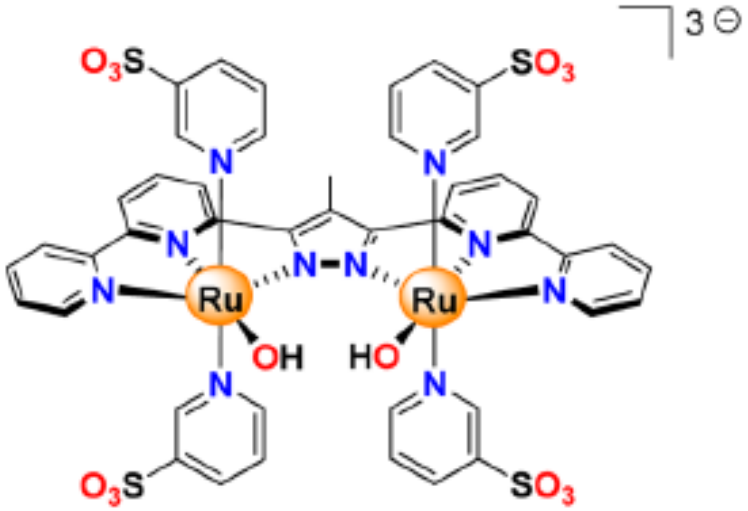
Ru-based Water Oxidation Catalysts

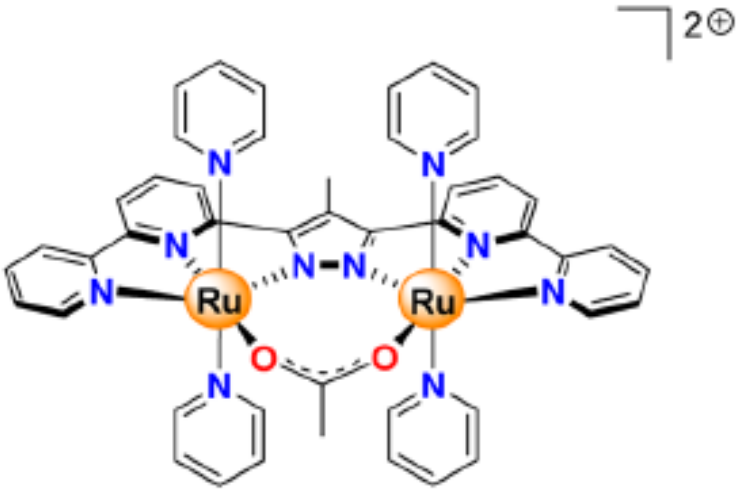


Blue-dimer

TON = 13.2 n_{O2}/n_{cat}



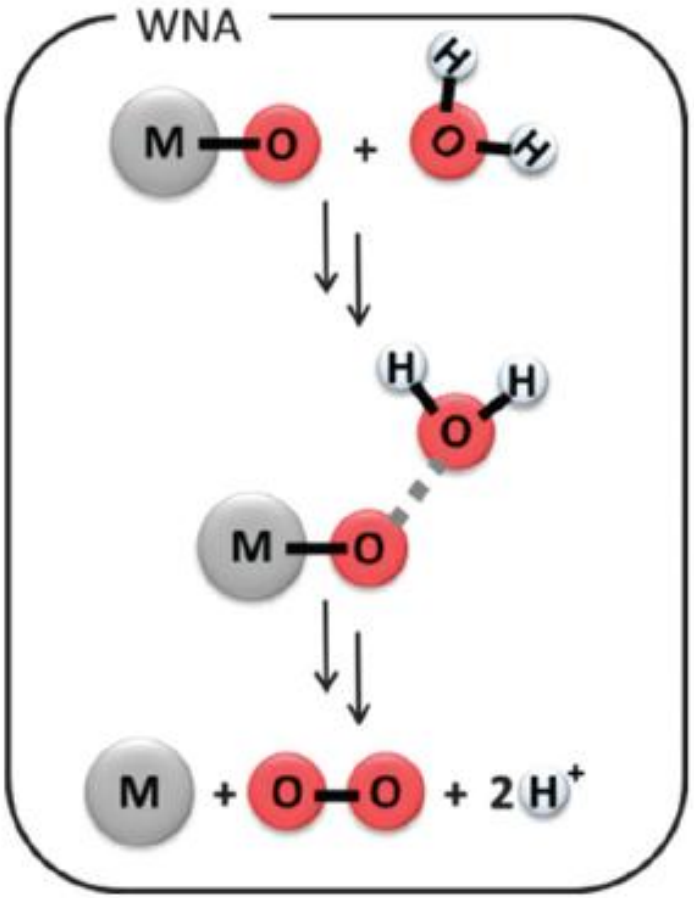




Akermark, B. et al., Chem. Rev. 2014, 114, 11863.

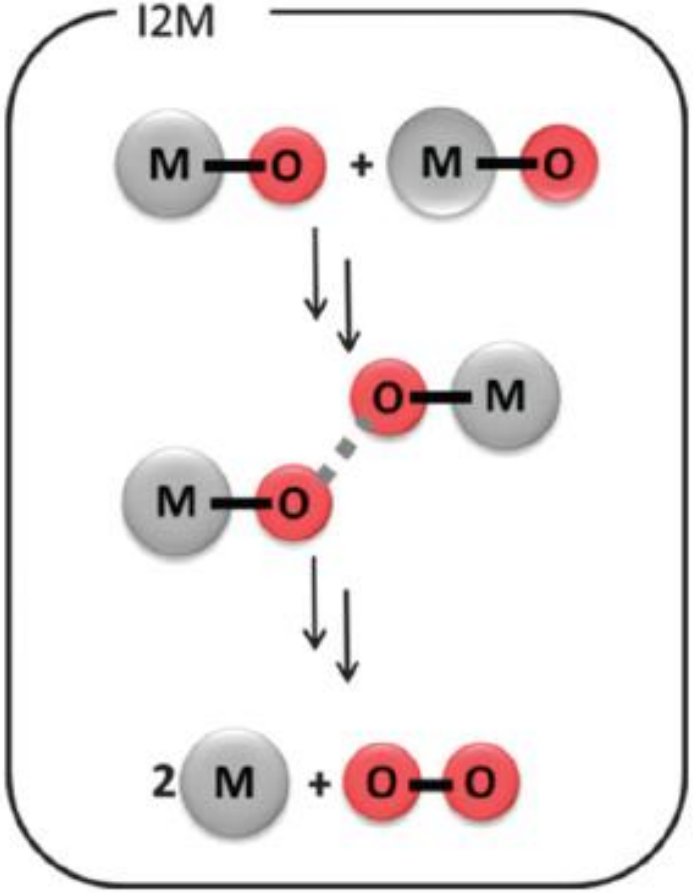
Possible mechanisms

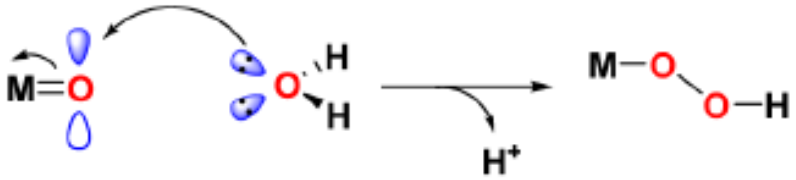
Water nucleophilic attack

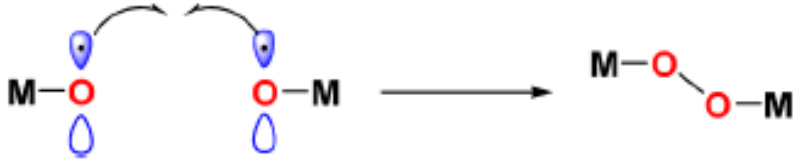


or

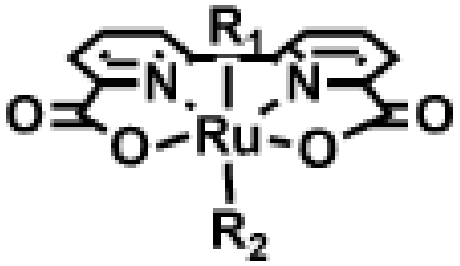
Interaction between two M-O units







Ru-based Water Oxidation Catalysts

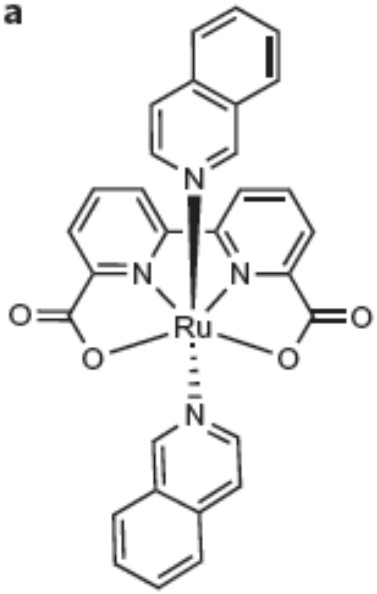


$R_1 = R_2 =$ 

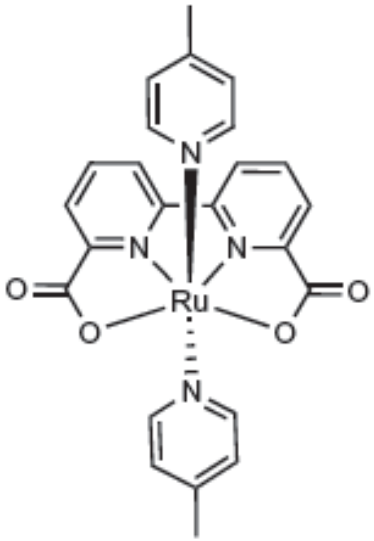
+ CAN [CAN]/[Ru] = 8000

TON = $5.0 \cdot 10^4$ n_{O2}/n_{cat} TOF = 300 s^{-1}

a

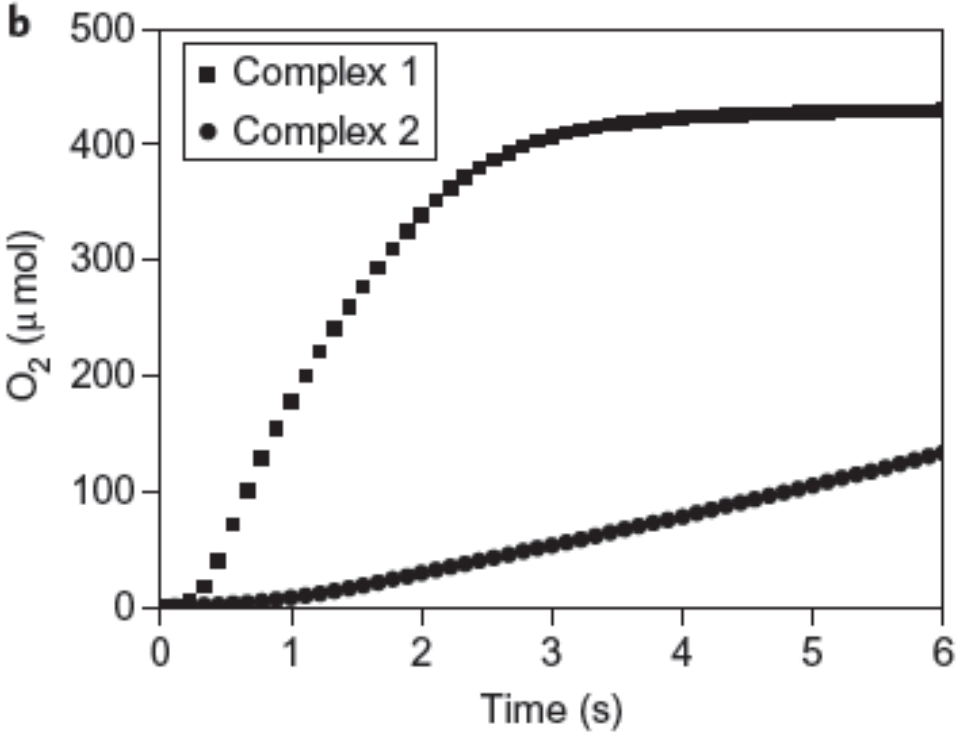


1

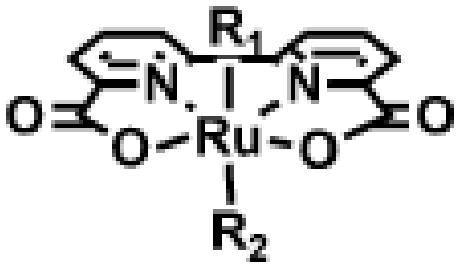


2

b

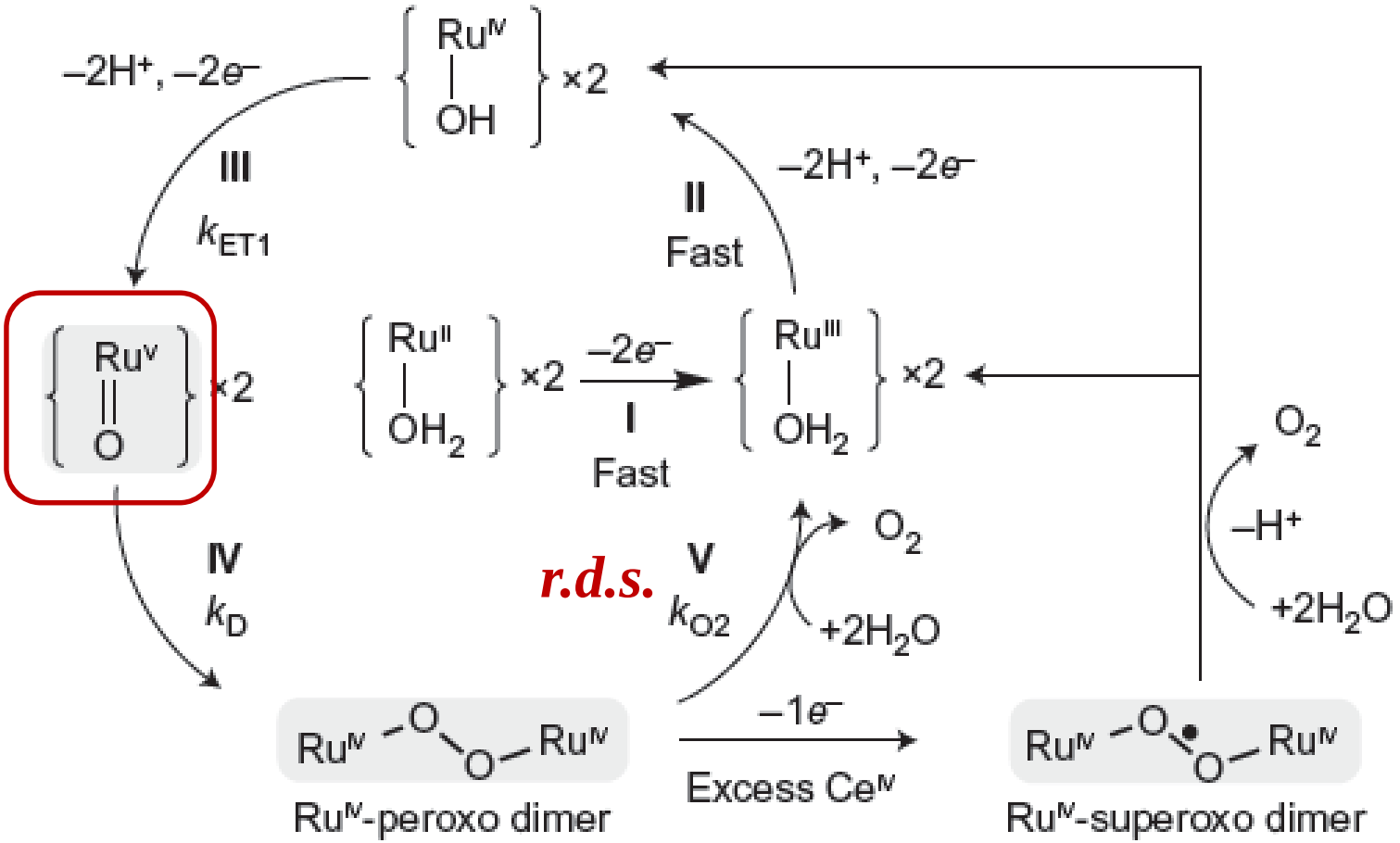


Possible mechanism

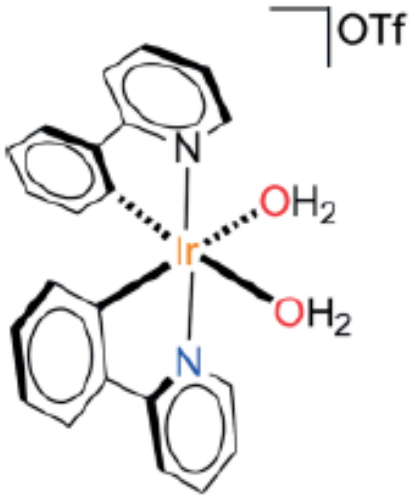


$R_1 = R_2 =$ 

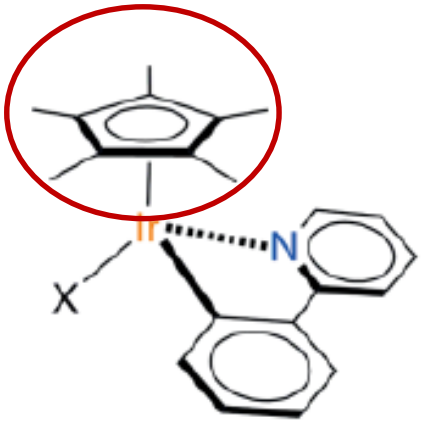
+ CAN [CAN]/[Ru] = 8000



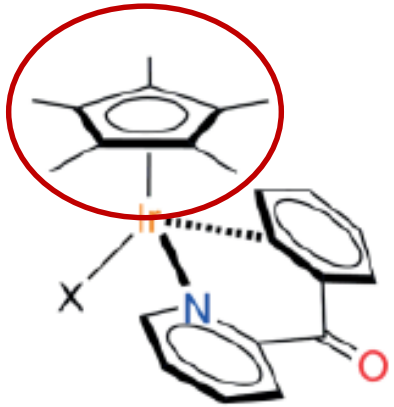
Ir-based Water Oxidation Catalysts



1, Bernhard 2008

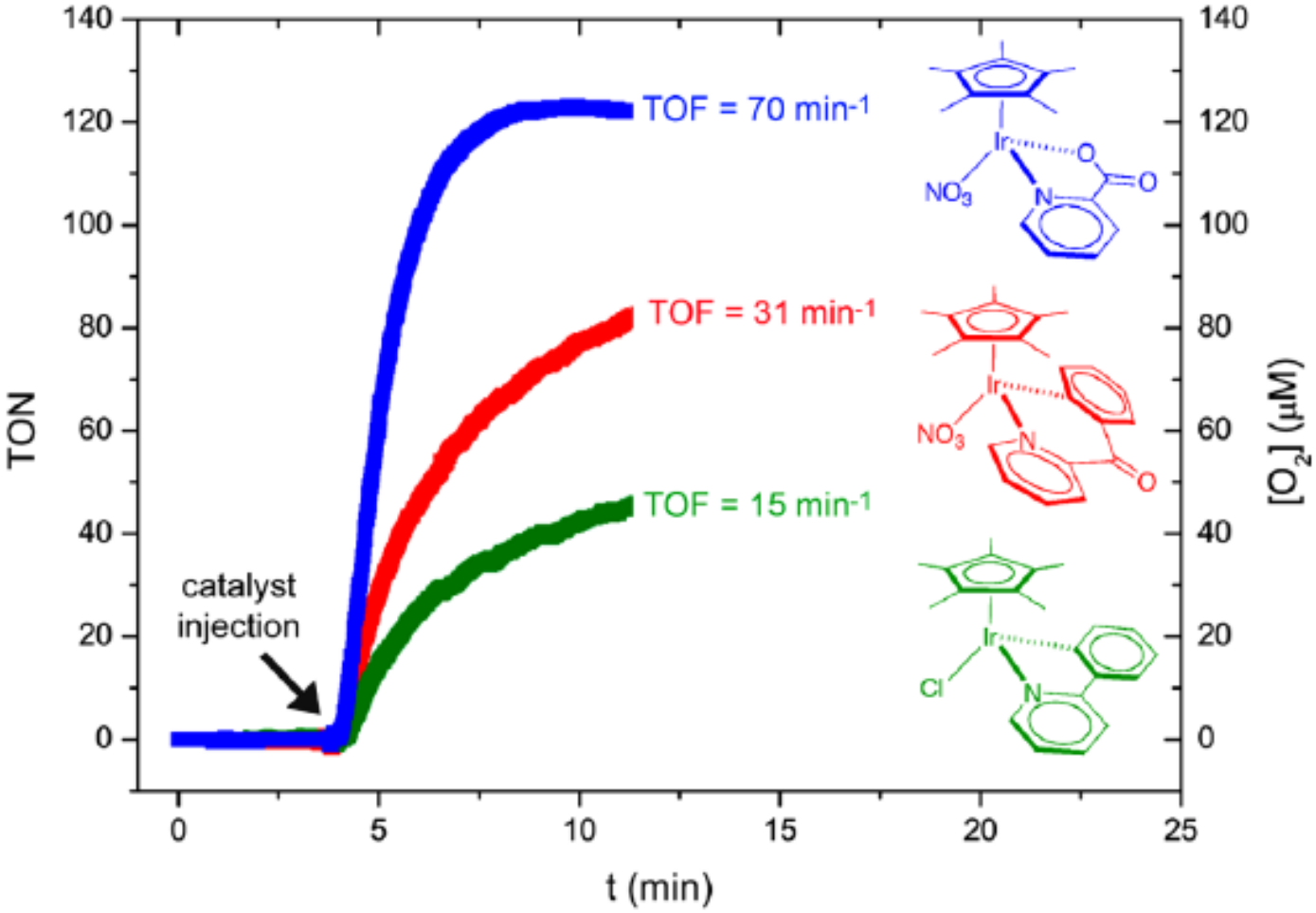


2, Crabtree 2009



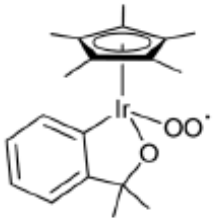
3, Macchioni 2010

Ir-based Water Oxidation Catalysts

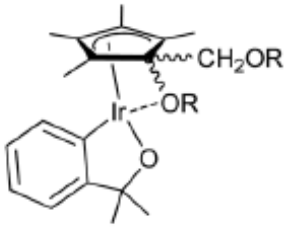


Reaction conditions: [CAN]/[Ir] = 40 000; pH = 1 with HNO_3; T = 25 °C; H_2O.

Possible mechanism

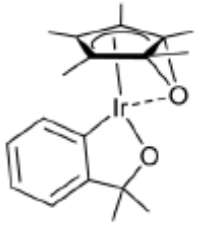


24

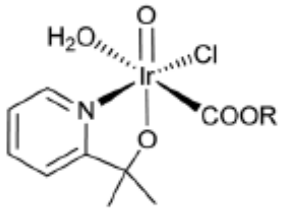


25

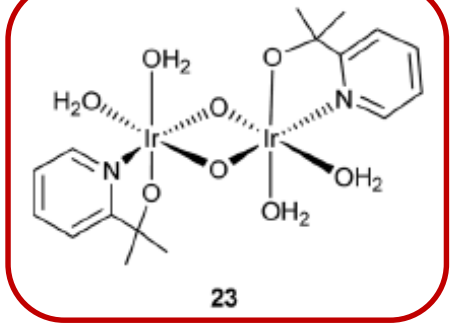
R = H or OH



26



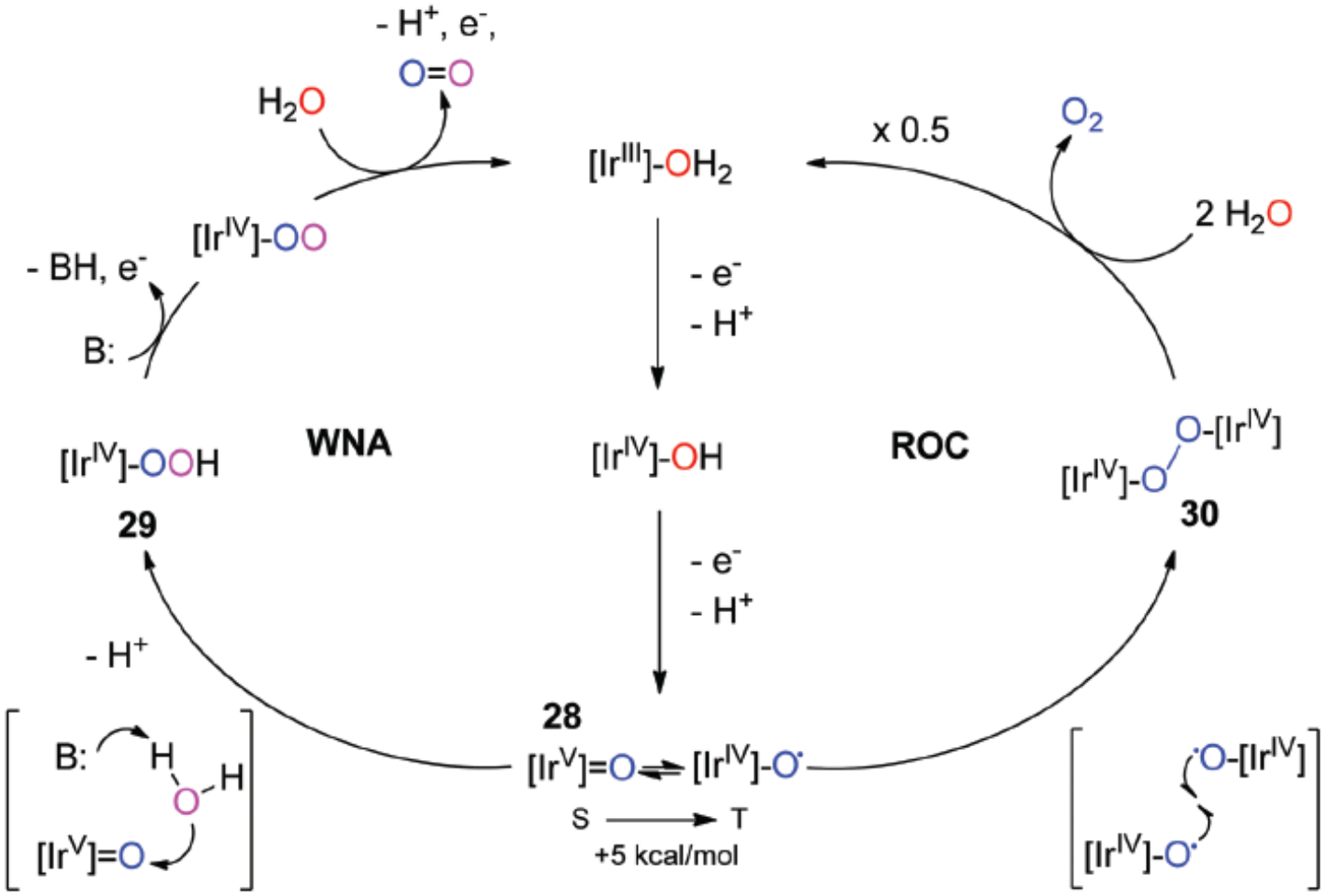
27



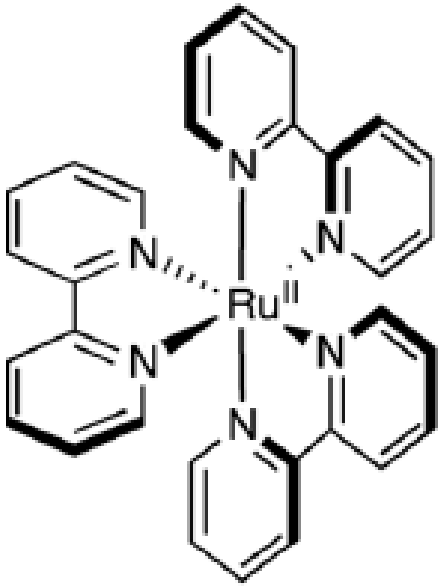
23

Cp intact* ⟹ *fully oxidized*

Possible mechanism



$[Ru(bpy)_3]^{2+}$: versatile visible light photocatalyst



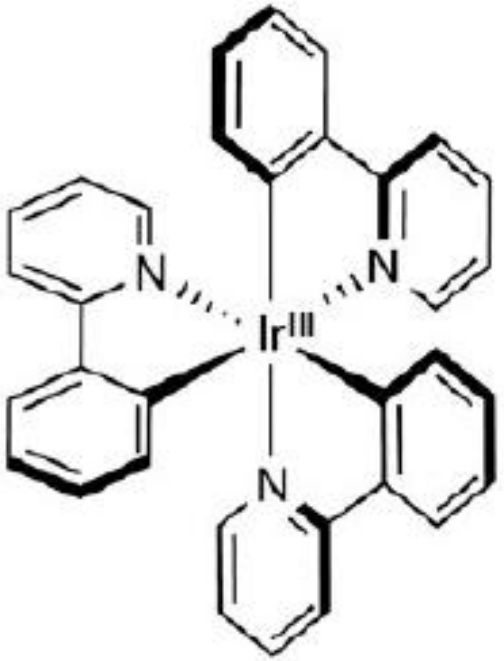
$Ru(bpy)_3^{2+}$

- Absorption at 452 nm (visible light)
- Stable, long-lived excited state (τ = 1100 ns)
- Single electron transfer (SET) catalyst
- Effective excited state oxidant and reductant

MacMillan, D.W.C. et al., Chem. Rev. 2013, 113, 5322:

> 30 applications in organic synthesis including reduction reactions, oxidation reactions, energy transfer.

[Ir(N-C)$_3$]: versatile photoredox catalyst

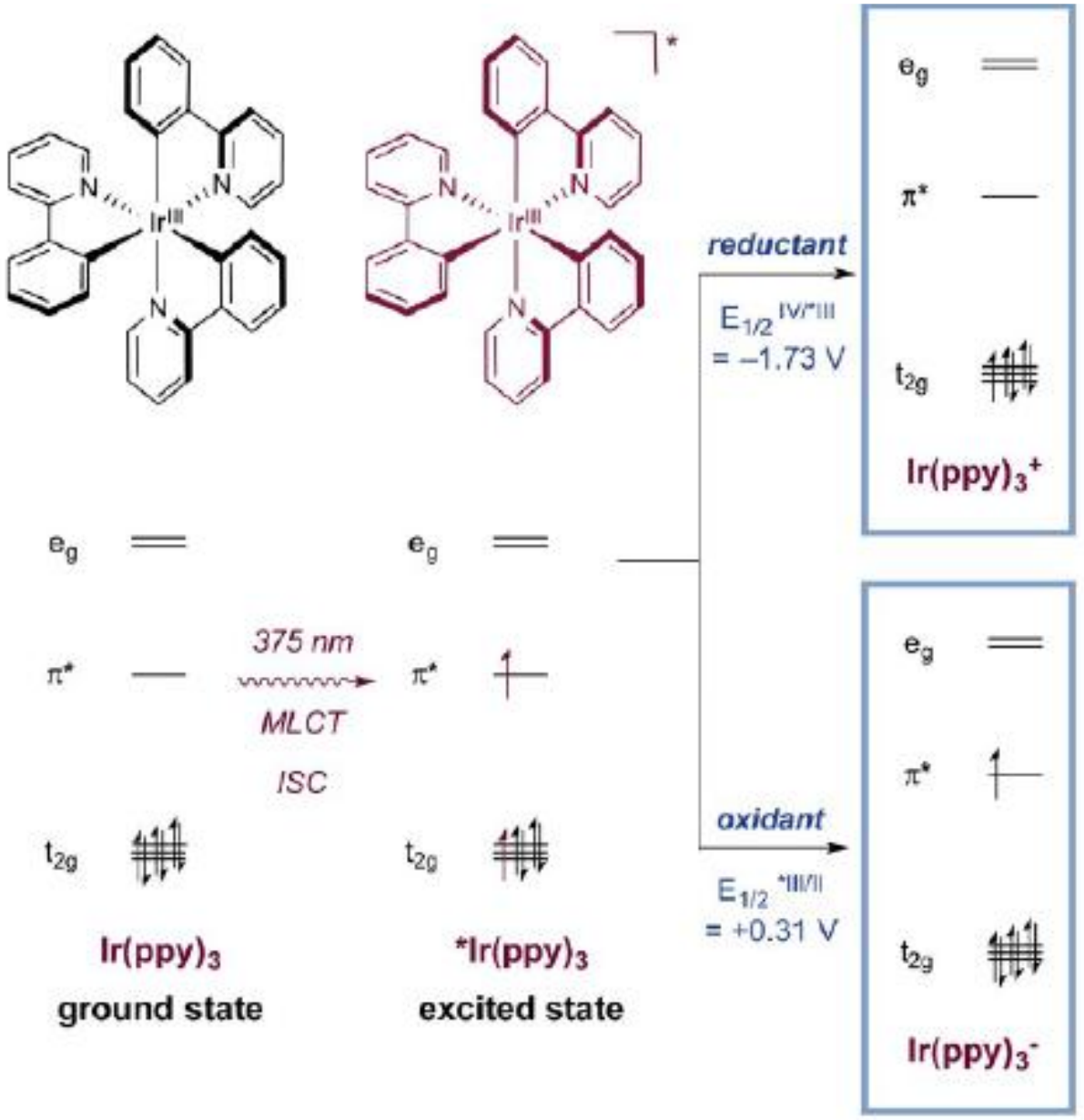


Ir(ppy)$_3$

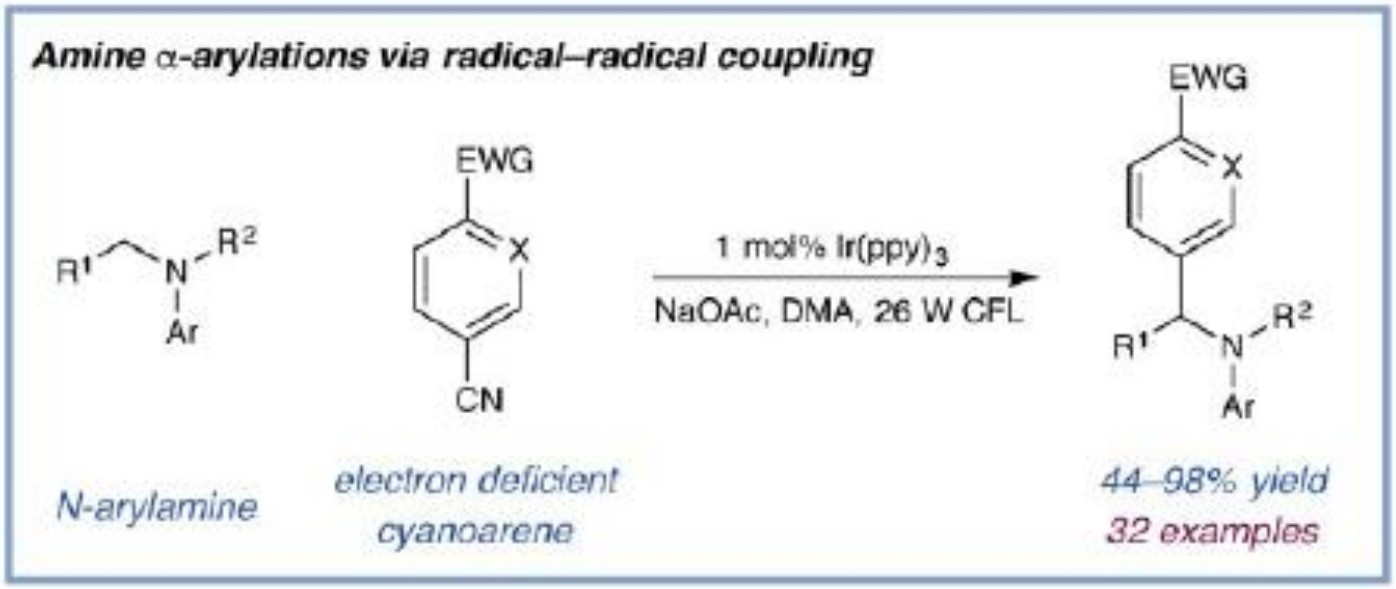
- Max absorption at 375 nm (visible light)
- Long-lived excited state (τ = 1.9 μs)
- Single-electron transfer catalyst
- Effective oxidant and reductant
- Triplet energy of 56 kcal mol^{-1}

MacMillan, D.W.C. et al., J. Org. Chem. 2016, 81, 6898.

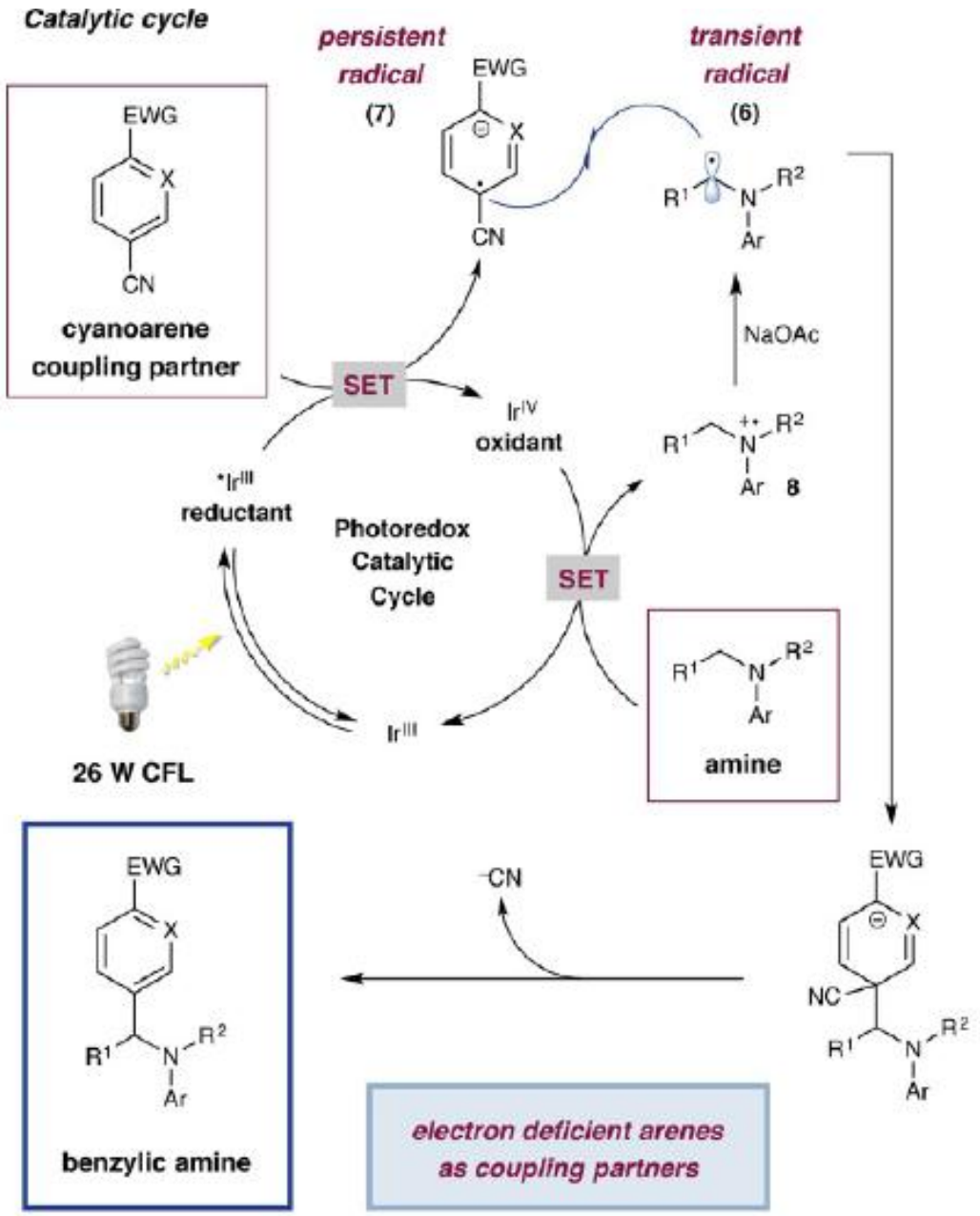
$[Ir(N\text{-}C)_3]$: simplified MO scheme



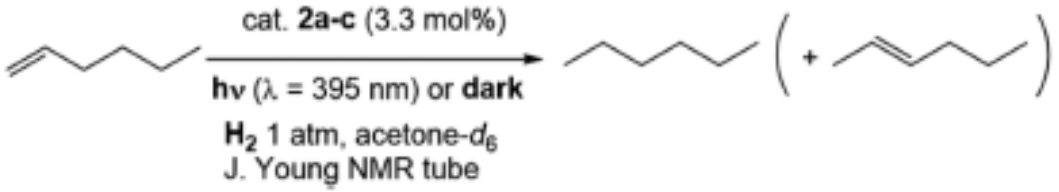
α-amino C-H arylation

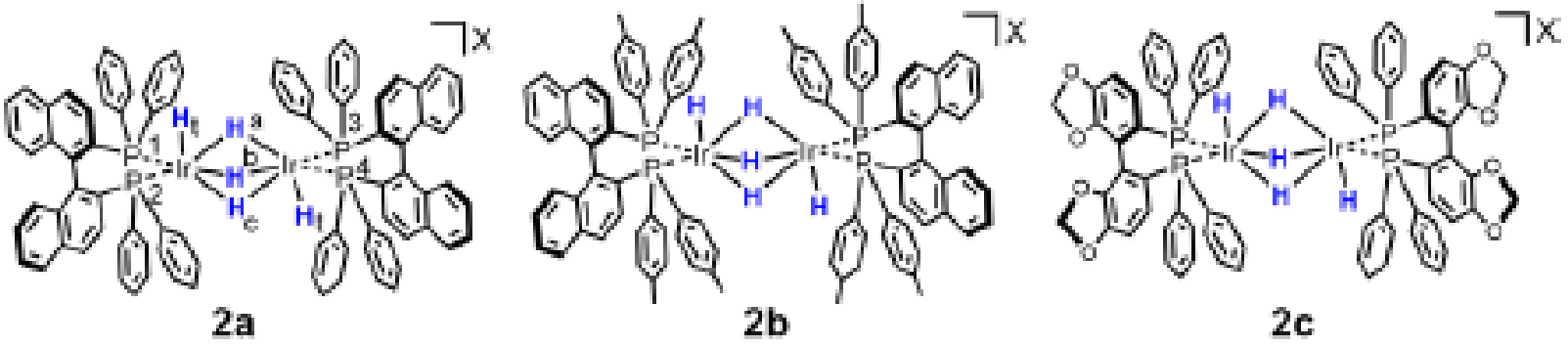


α-amino C-H arylation



Photocatalytic hydrogenation of 1-hexene





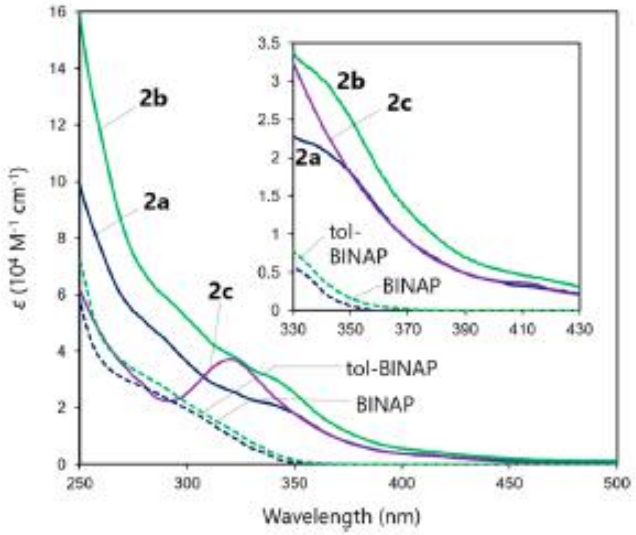
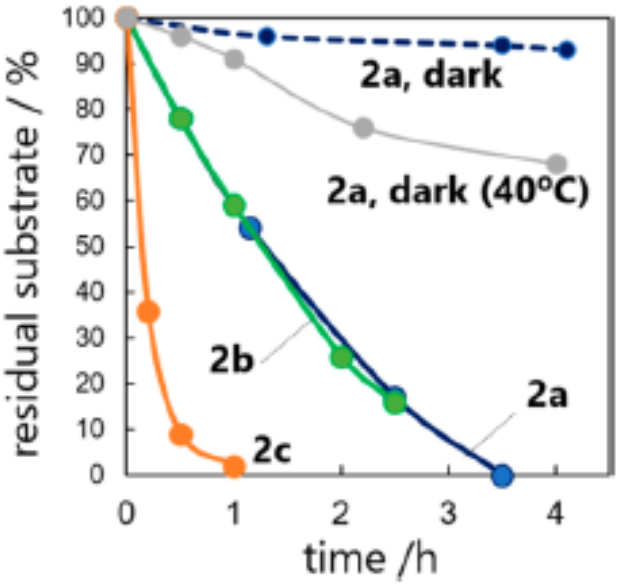


Figure 1. UV–vis absorption spectra of complexes 2a–c and the BINAP ligands.



Inagaki, A. et al., Organometallics 2019, 38, 2408.