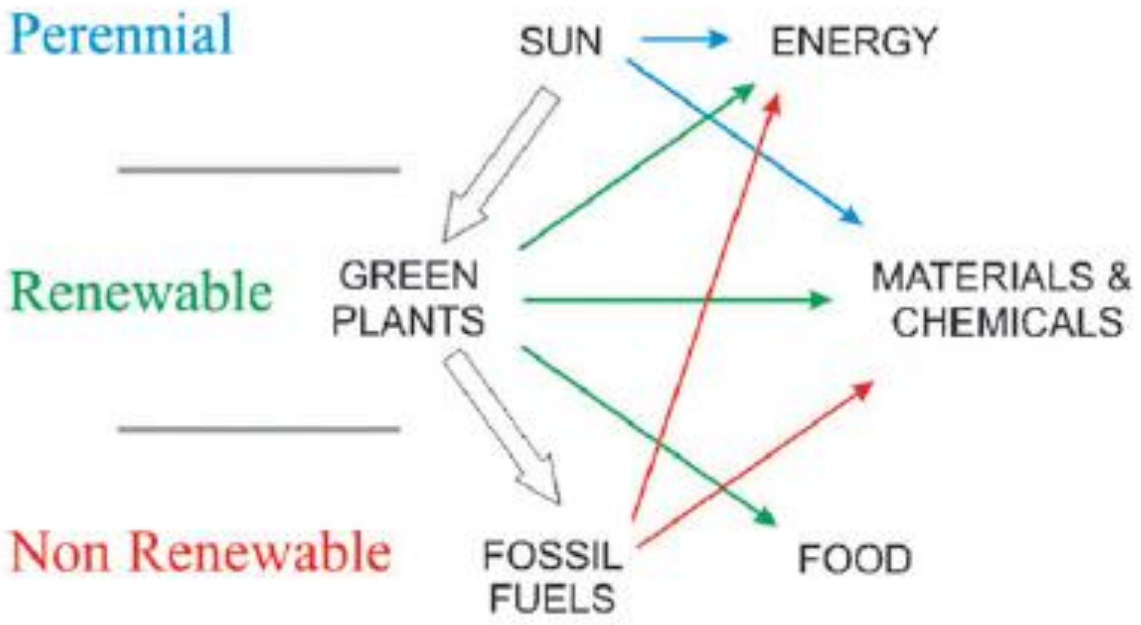
Photocatalysis and sustainability

«…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:

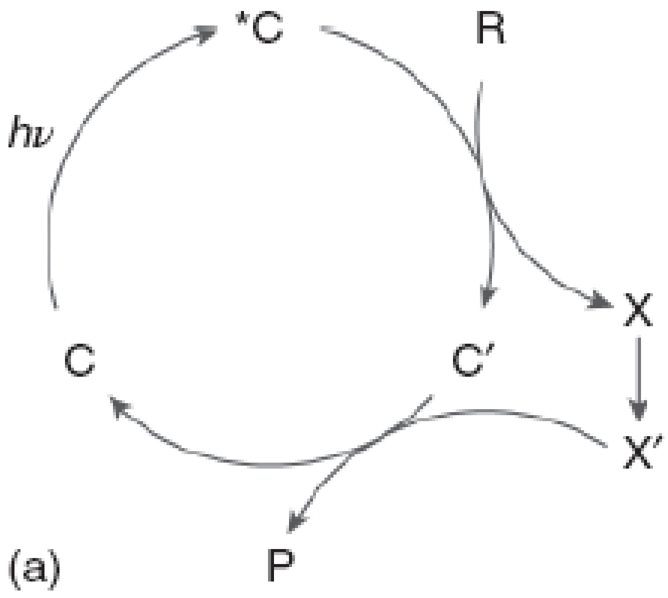
- ✓ **Diluted solutions;**
- ✓ **The light source: Solar Light *vs* Artificial sources of Visible Light.**

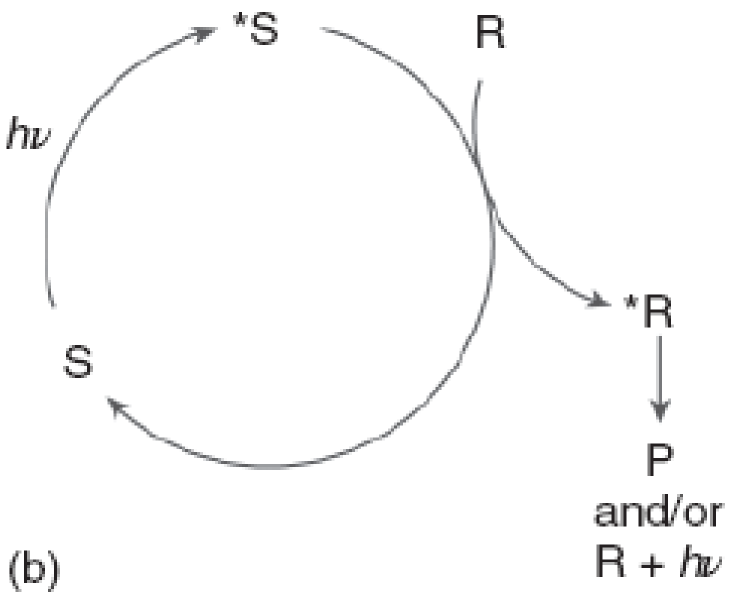
Photocatalysis

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

Photocatalysis

Energy-transfer photosensitization



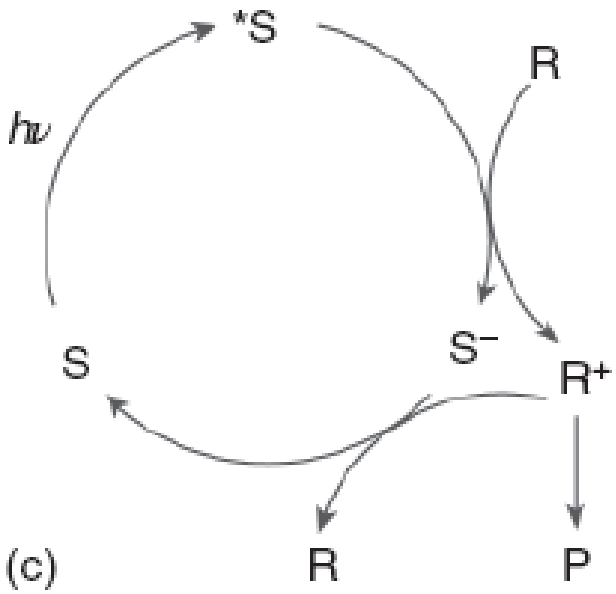


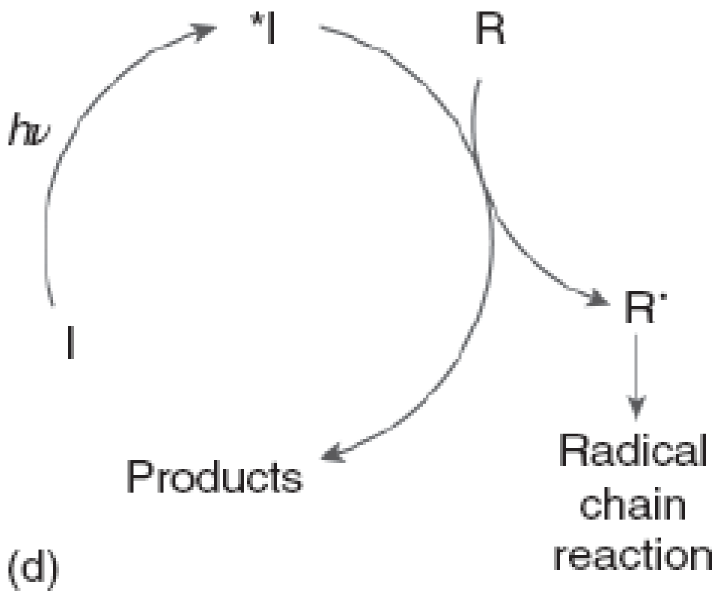
Photocatalysis

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

Electron-transfer photosensitization

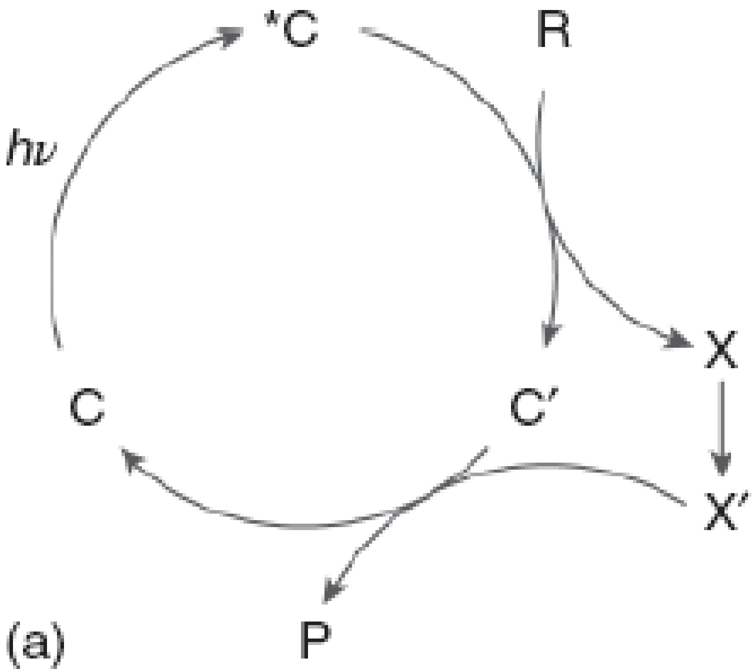
Photoinduced chain reaction





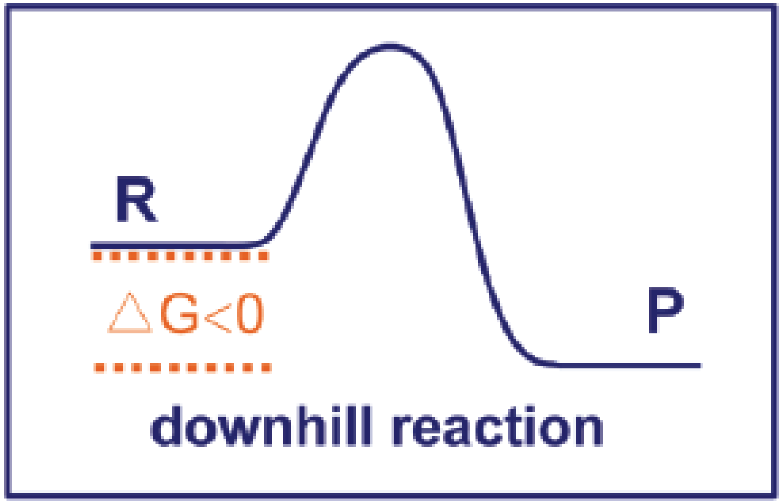
Photocatalysis

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

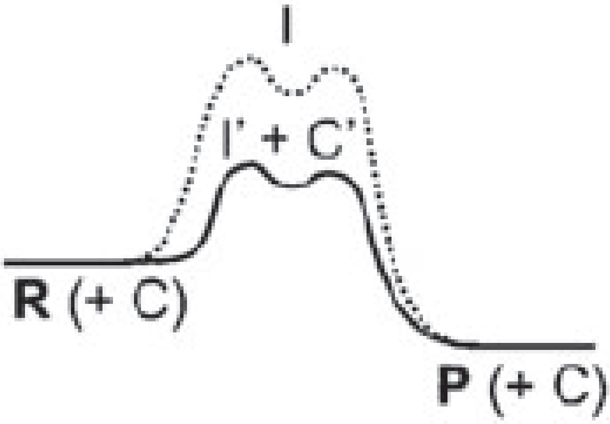


Photocatalysis: Thermodynamic aspects

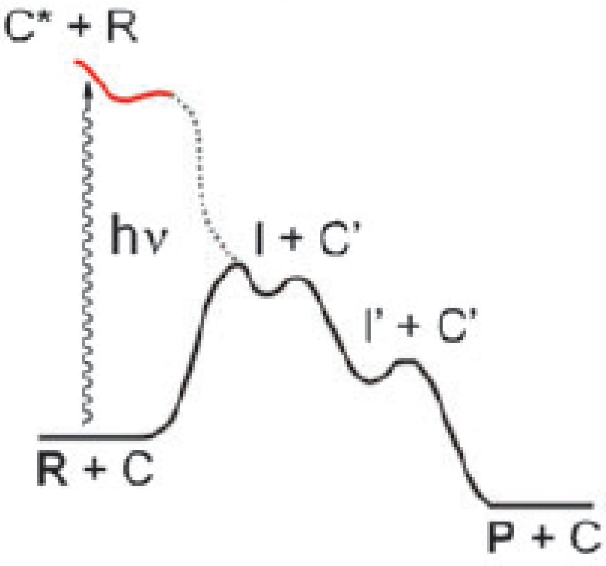
Spontaneous reactions



Thermal reaction

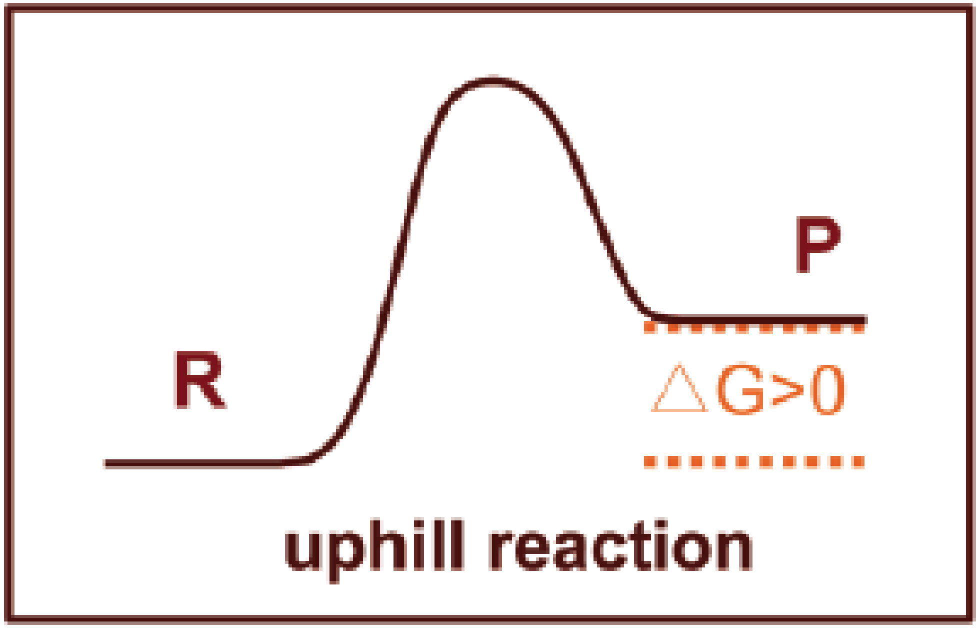


Photochemical reaction



Photocatalysis: Thermodynamic aspects

Non-Spontaneous reactions

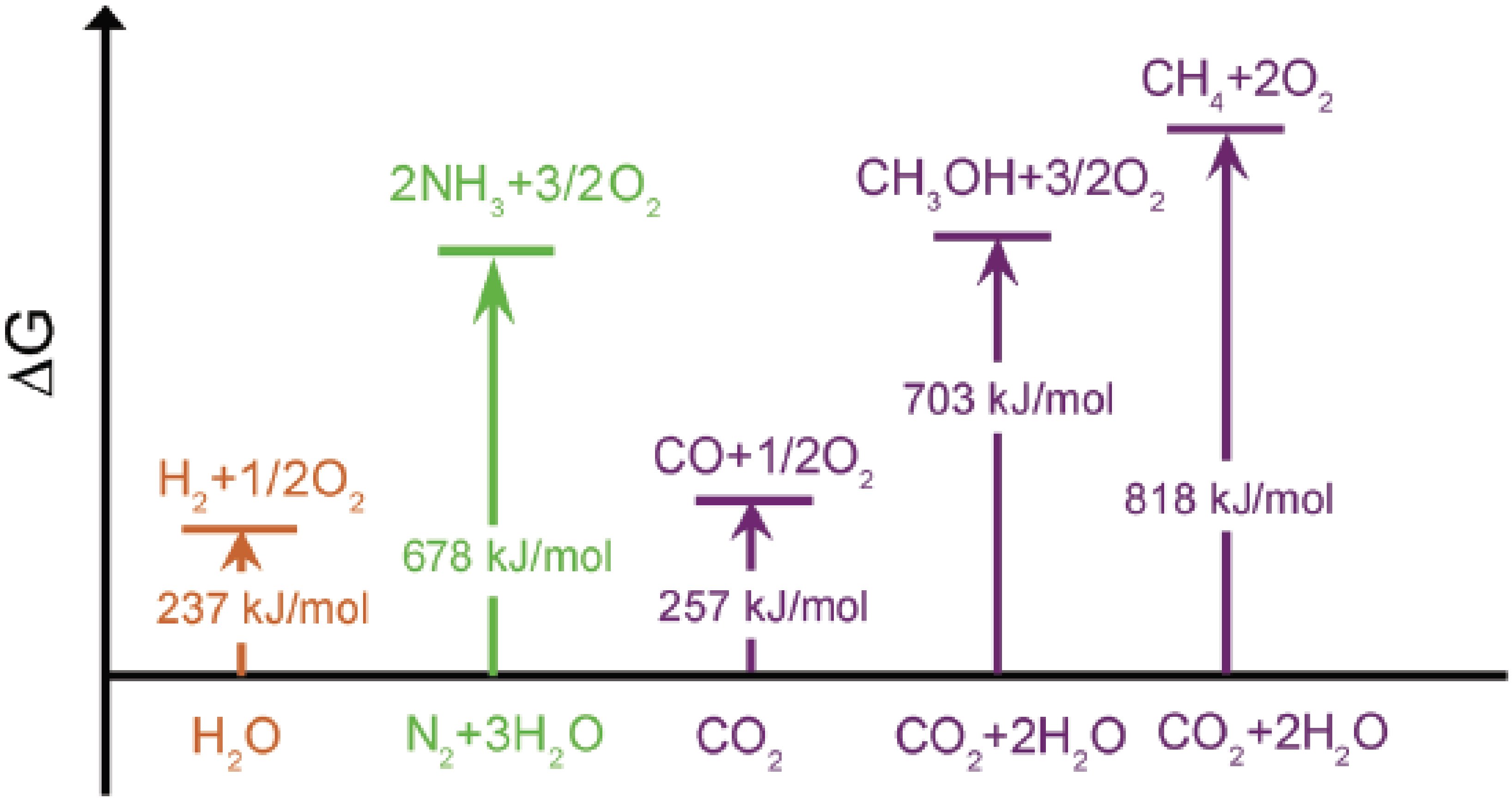


Broader approach

«.. 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.»

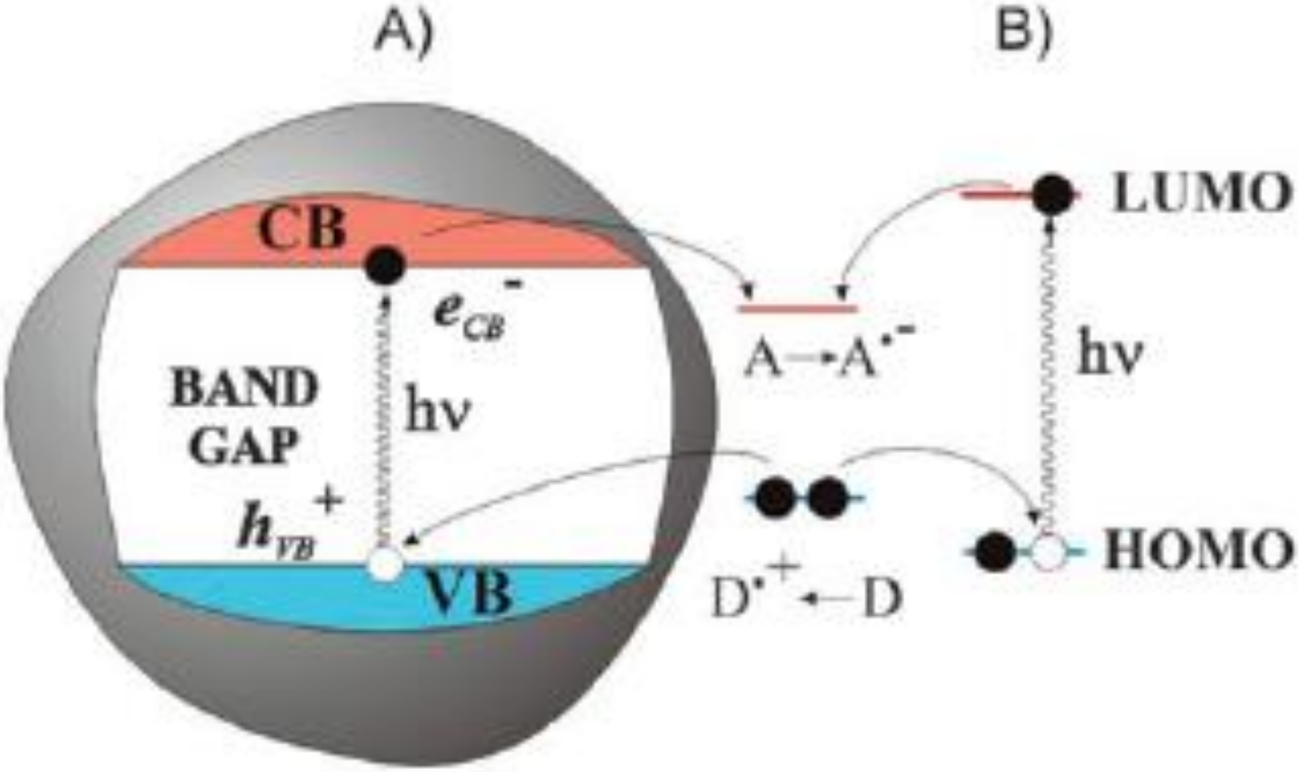
R. Noyori *Tetrahedron* 2010, *66*, 1028.

Thermodynamically uphill reactions



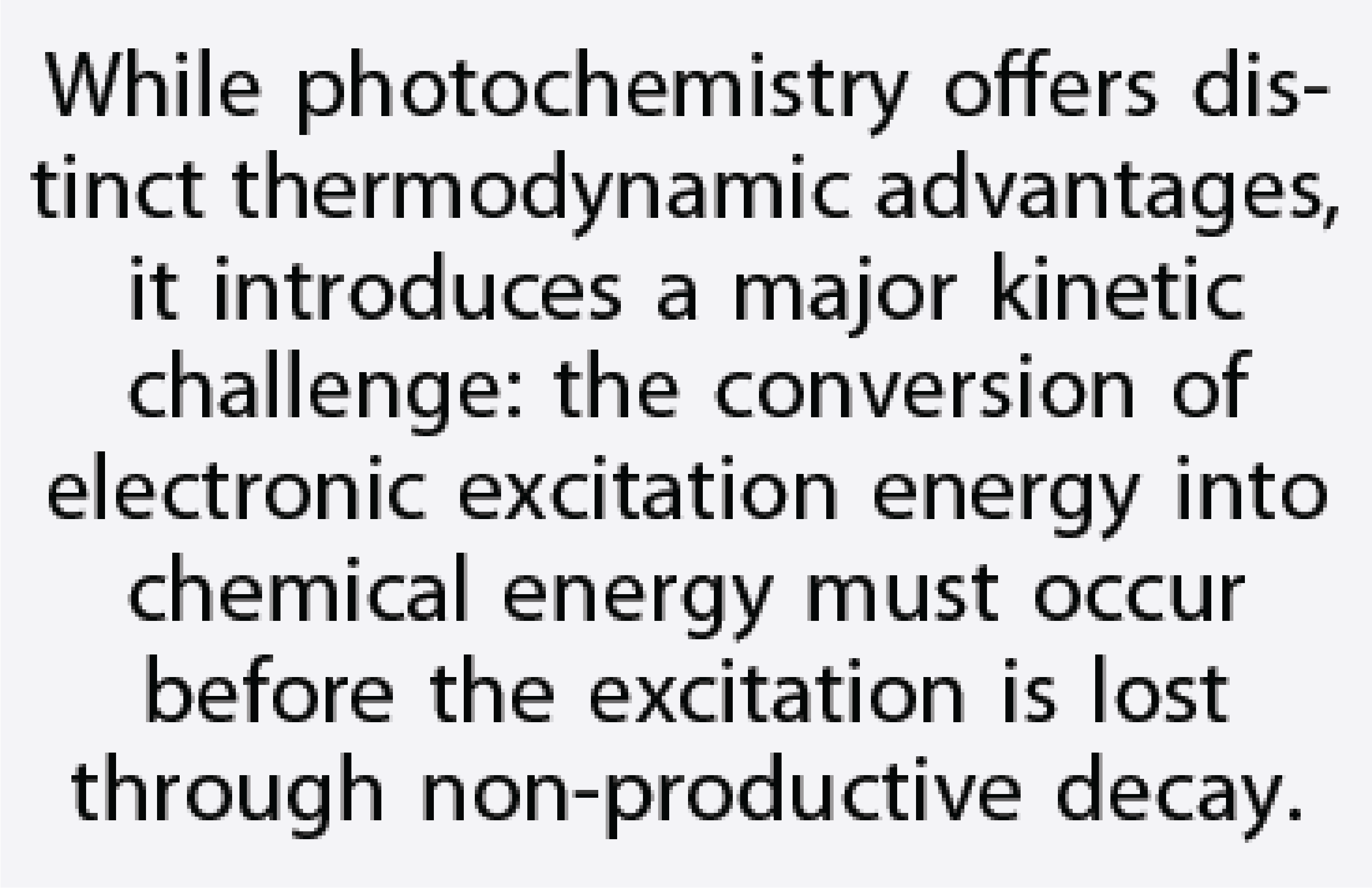
Photocatalysis at semiconductor particles or molecules

Heterogeneous photocatalysis *vs* homogeneous photocatalysis



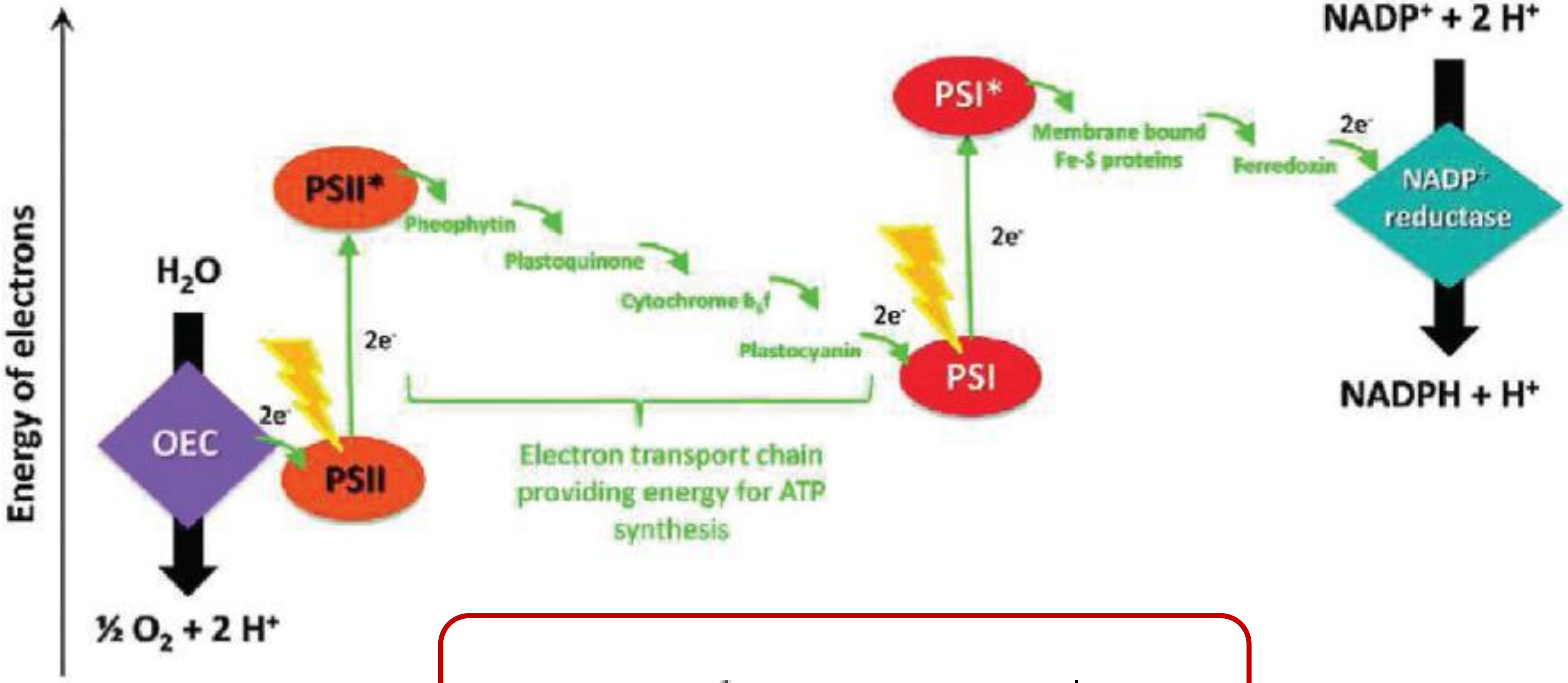
TON **TOF** **Φ**

Photocatalysis



While photochemistry offers distinct thermodynamic advantages, it introduces a major kinetic challenge: the conversion of electronic excitation energy into chemical energy must occur before the excitation is lost through non-productive decay.

Photosynthesis in nature



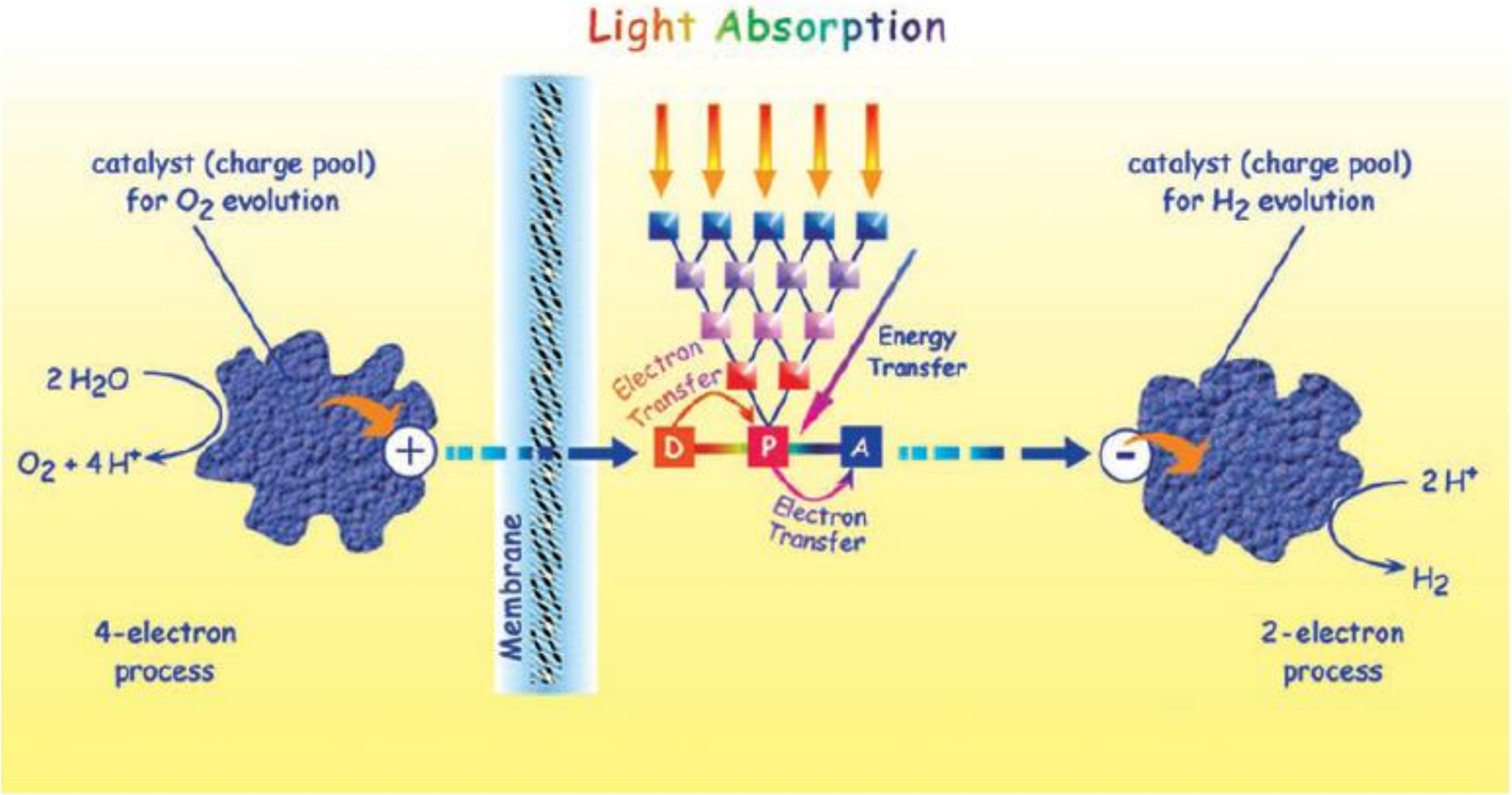
$$\boxed{2\mathrm{H_2O} + 4h\nu \rightarrow \mathrm{O_2} + 4\mathrm{H^+} + 4\mathrm{e^-}}$$

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

Artificial Photosynthesis

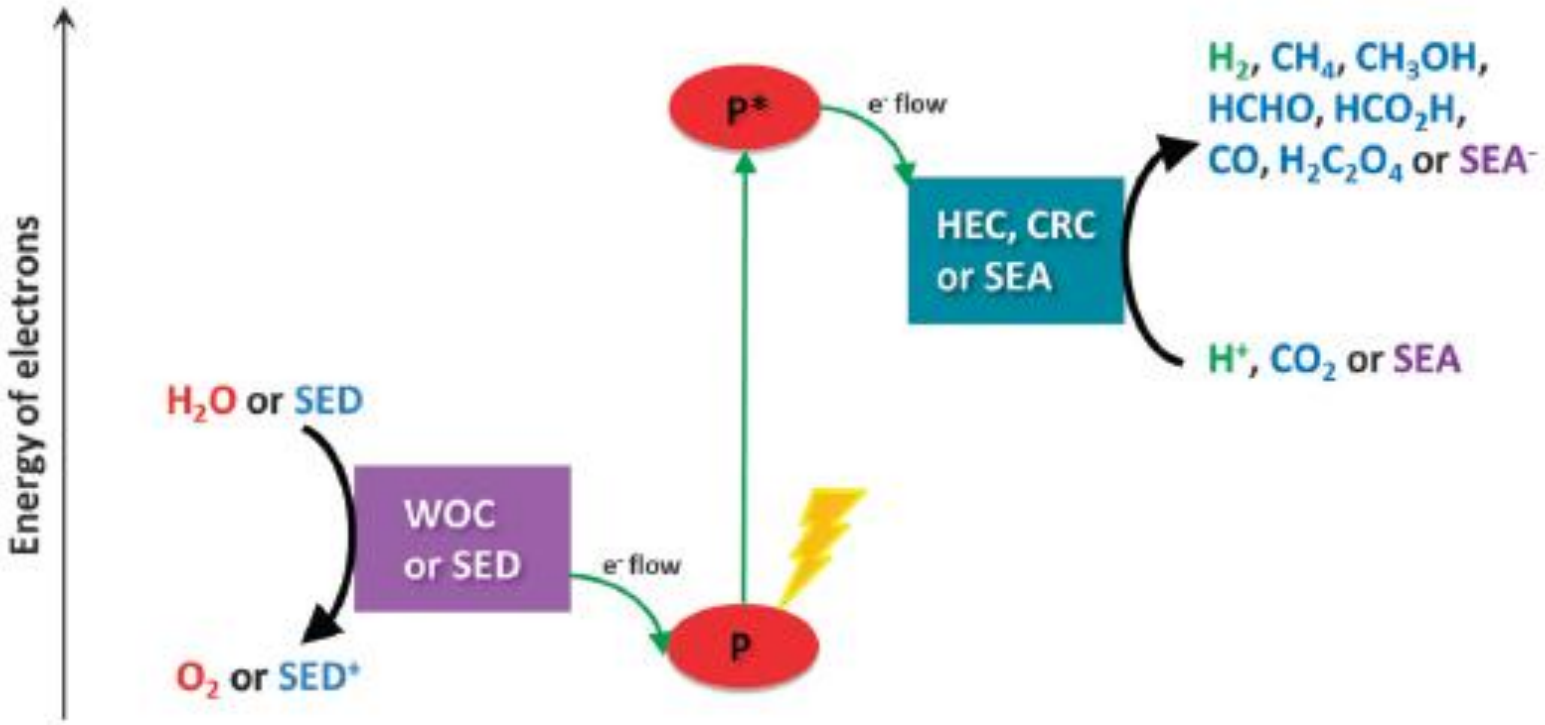
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

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

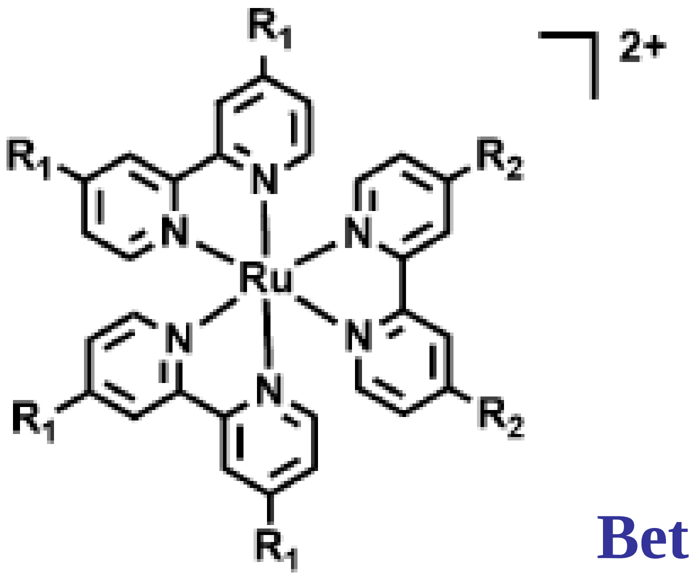


Artificial Photosynthesis

$$H_2O \xrightarrow[\text{photocatalyst}]{\text{solar energy}} H_2 + 1/2O_2$$

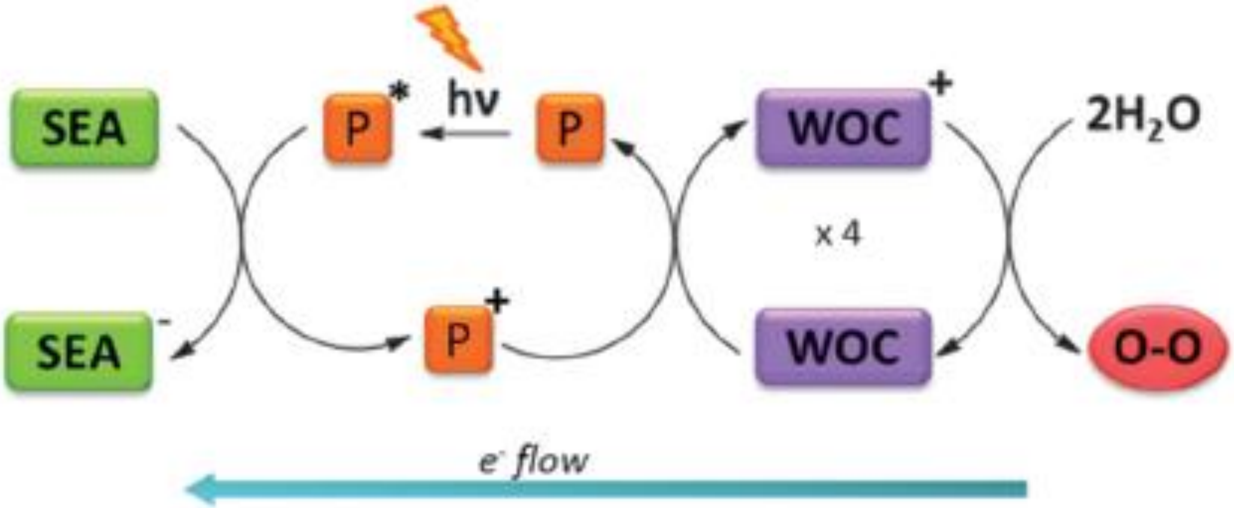


Photosensitizer



- 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

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

SEA più utilizzati

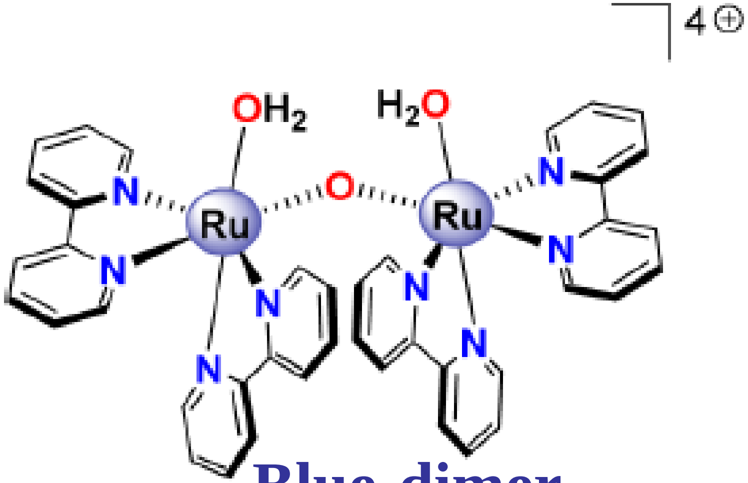
CAN $4Ce^{4+} + 4e^- \rightarrow 4Ce^{3+}$ $E^0 = 1.72\ V$

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

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

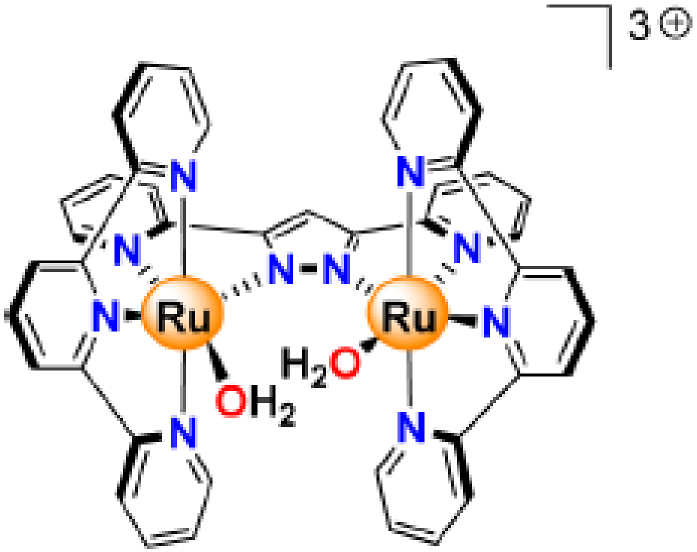
$$2H_2O + nOx \rightarrow 4H^+ + O_2 + nRed$$

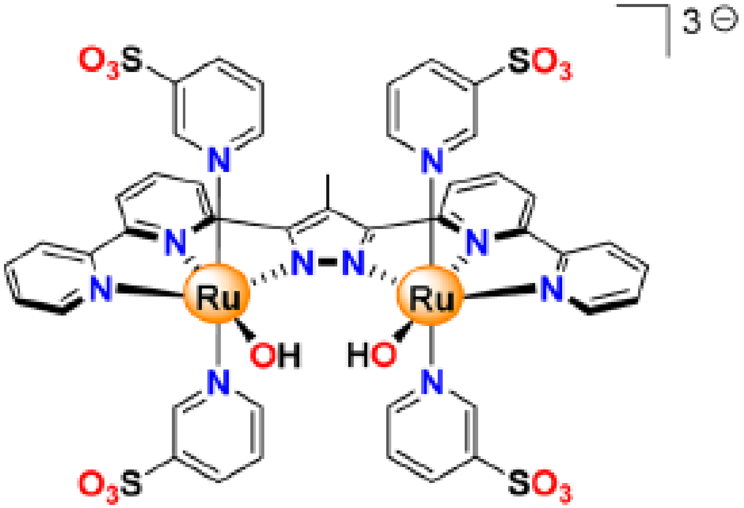
Ru-based Water Oxidation Catalysts

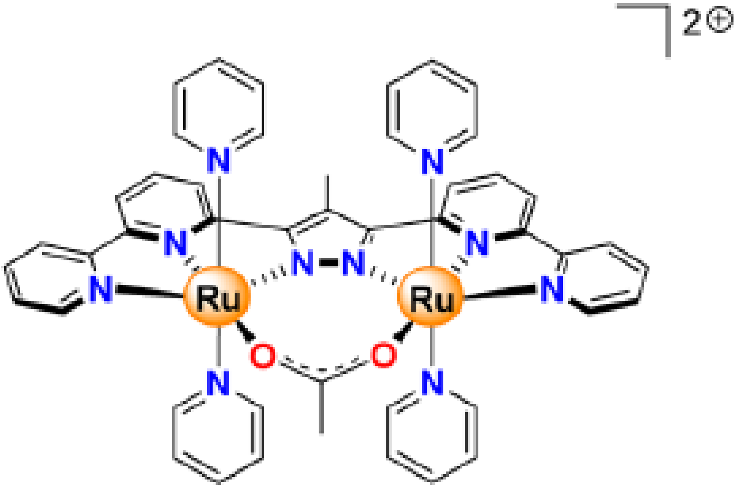


Blue-dimer

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



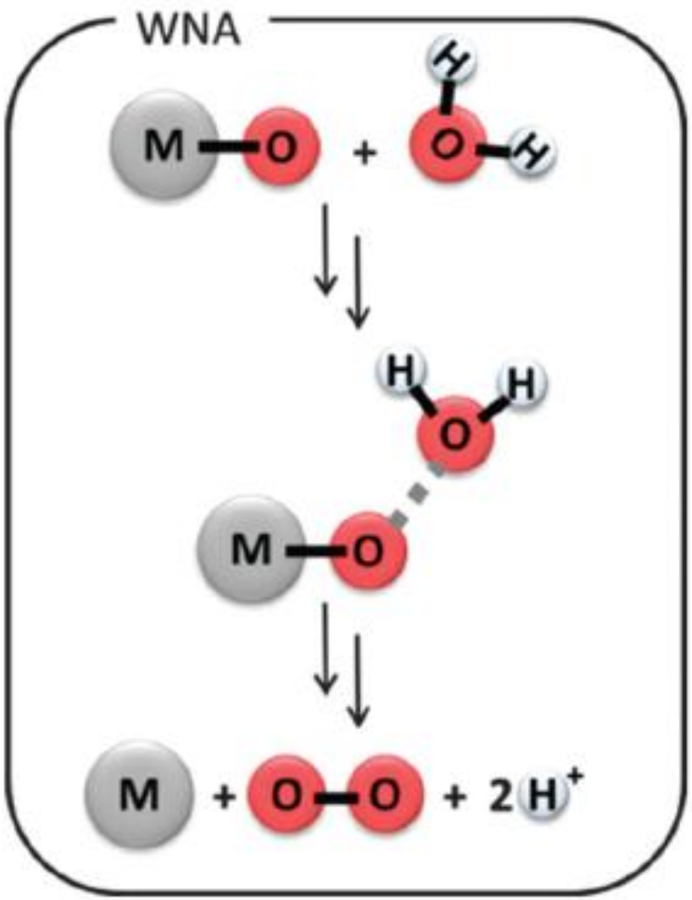


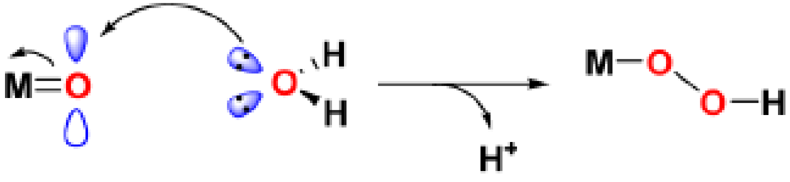


Akermark, B. et al., Chem. Rev. 2014, 114, 11863.

Possible mechanisms

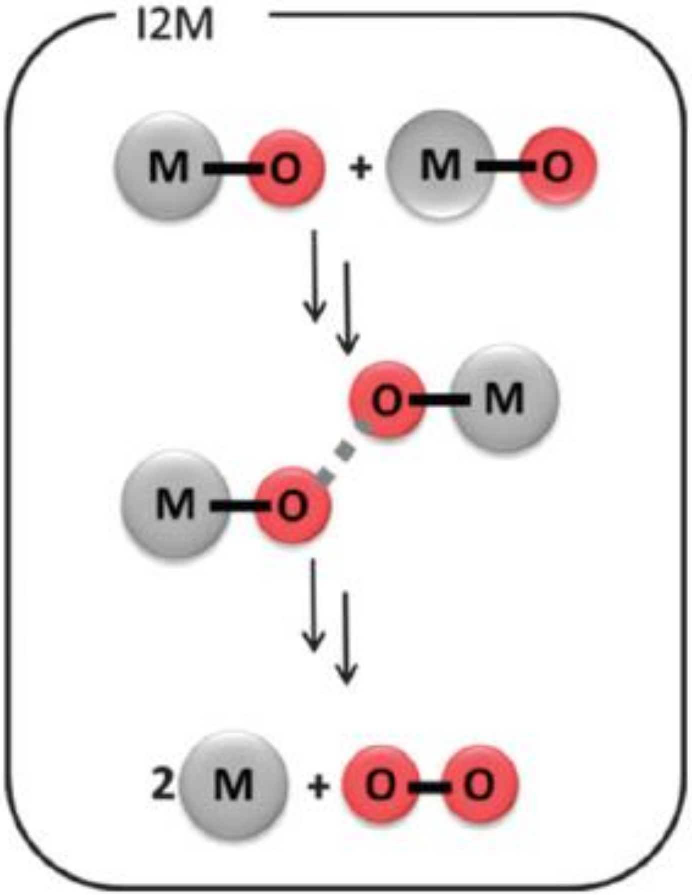
Water nucleophilic attack



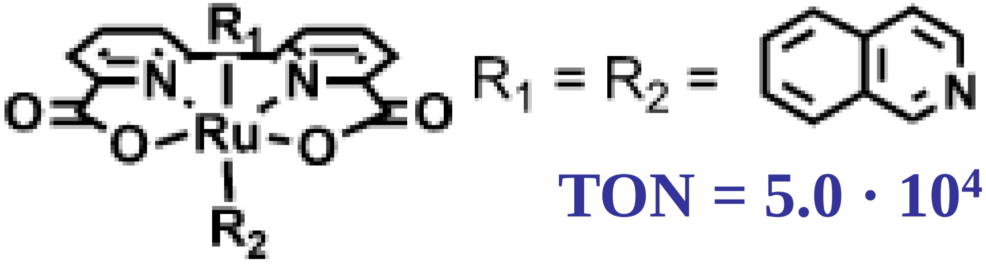


or

Interaction between two M-O units

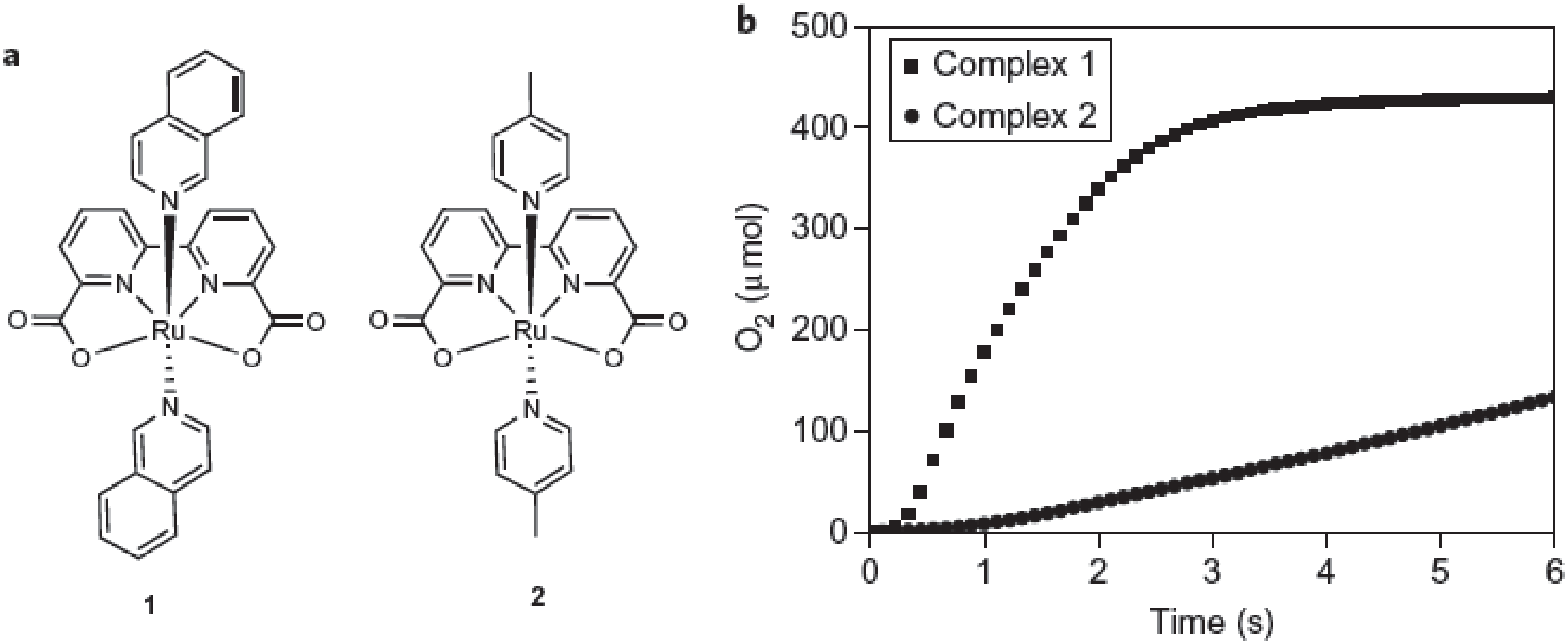


Ru-based Water Oxidation Catalysts

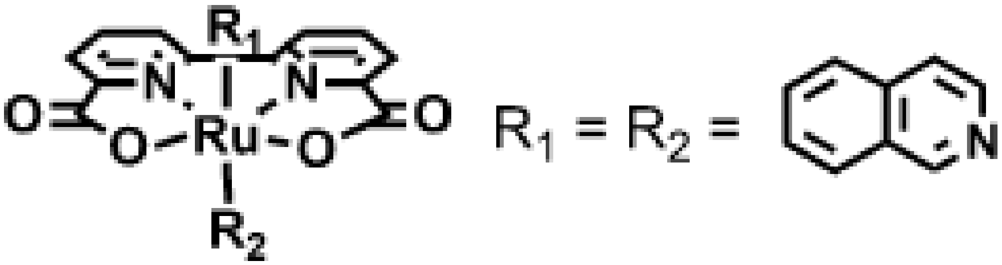


+ CAN [CAN]/[Ru] = 8000

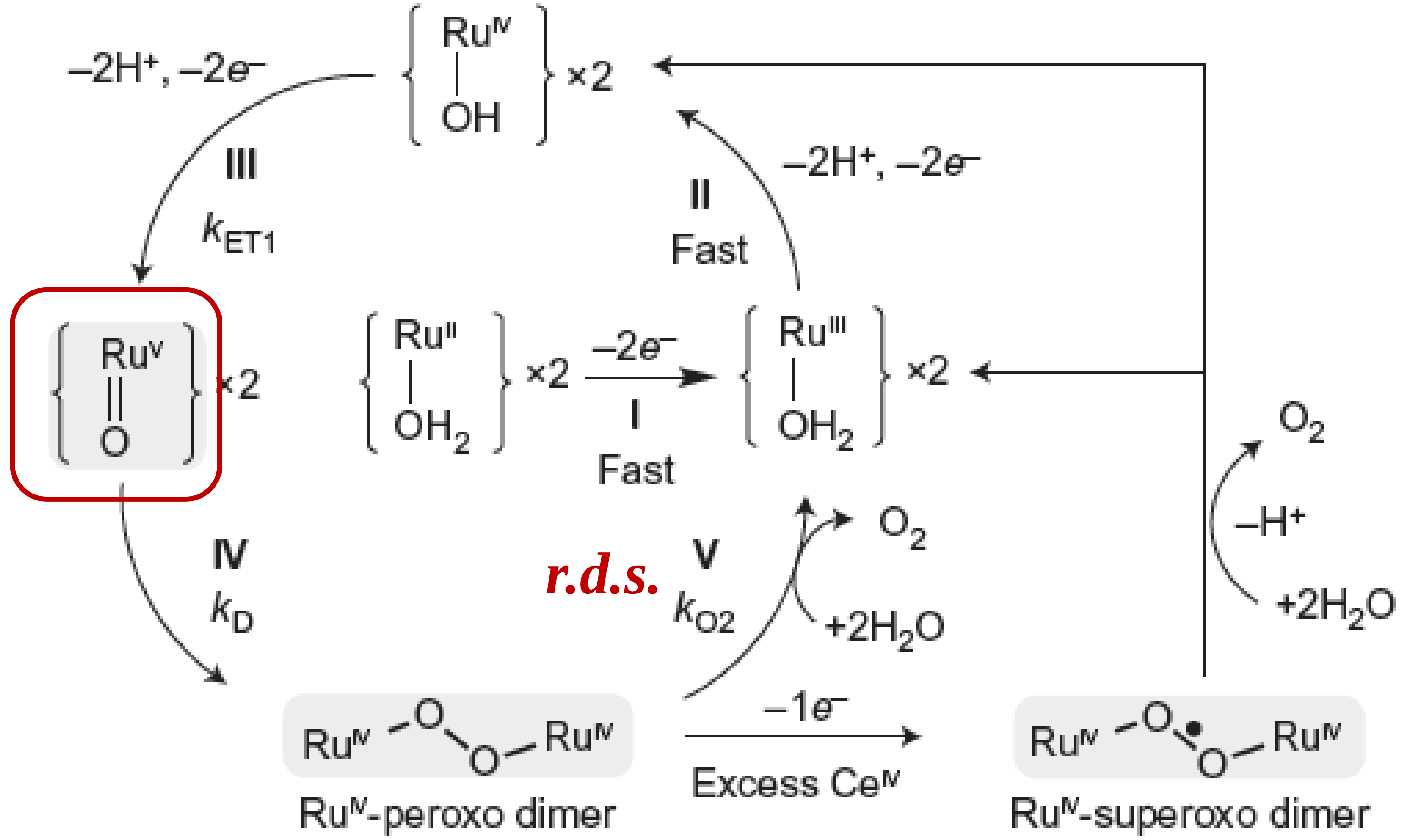
TON = $5.0 \cdot 10^4$ n_{O2}/n_{cat} TOF = 300 s^{-1}



Possible mechanism

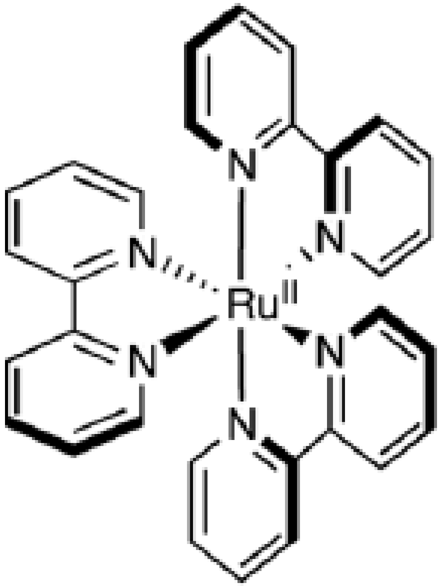


+ CAN [CAN]/[Ru] = 8000



r.d.s.

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



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

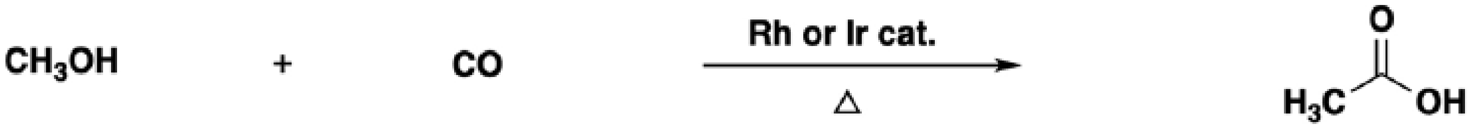
- Absorption at 452 nm (visible light)
- Stable, long-lived excited state ($\tau = 1100$ ns)
- Single electron transfer (SET) catalyst
- Effective excited state oxidant and reductant

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

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

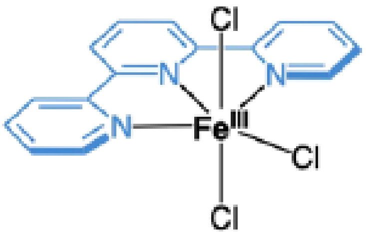
The synthesis of acetic acid

The carbonylation of methanol



The aerobic carbonylation of methane

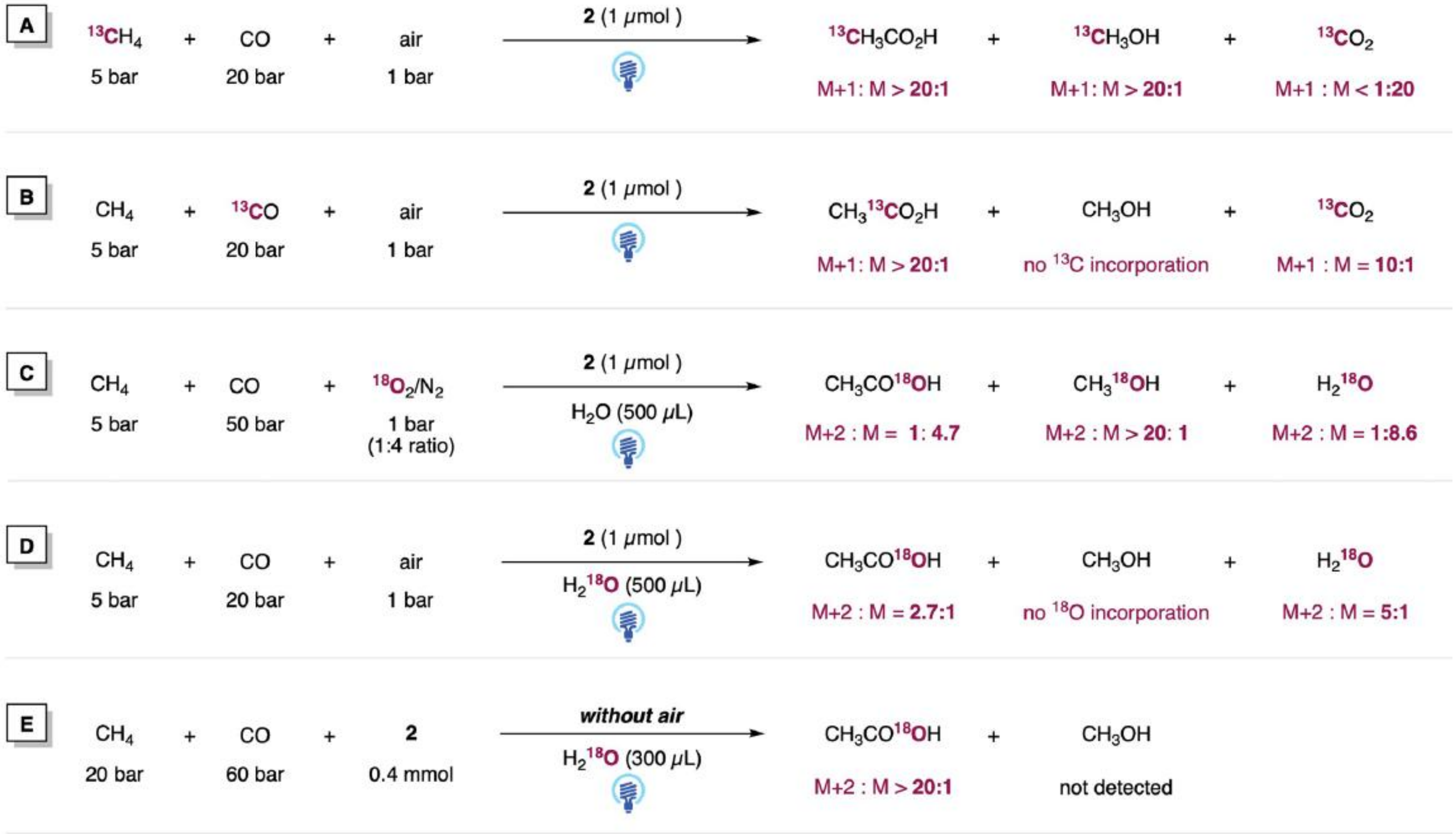
$$\underset{2\ \text{bar}}{CH_4} + \underset{5\ \text{bar}}{CO} + \underset{1\ \text{bar}}{\text{air}} \xrightarrow[\substack{NH_4Cl\ (50\ \mu mol),\ HFIP\ (10\ mL) \\ LEDs\ (400\ nm,\ 0.37\ W/cm^2),\ r.t.,\ 8\ h}]{\textbf{photocatalyst}} CH_3CO_2H$$

photocatalyst	**C2 product**		**C1 product**		**Selectivity**
1 μmol	CH_3CO_2H	$CH_3CO_2CH(CF_3)_2$	CH_3OH	HCO_2H	**C2/C1**
	**241**	**86**	**7**	**21**	**12:1**

Liu, P.; Zuo, Z. et al., J. Am. Chem. Soc. 2025, 147, 1440.

Isotope labelling experiments

Scheme 1. Isotope labelling experiments[a]



A

$$^{13}CH_4 + CO + air \xrightarrow[\text{💡}]{\mathbf{2}\ (1\ \mu mol)} {}^{13}CH_3CO_2H + {}^{13}CH_3OH + {}^{13}CO_2$$

$^{13}CH_4$ 5 bar; CO 20 bar; air 1 bar

$^{13}CH_3CO_2H$: M+1: M > **20:1**; $^{13}CH_3OH$: M+1: M > **20:1**; $^{13}CO_2$: M+1 : M < **1:20**

B

$$CH_4 + {}^{13}CO + air \xrightarrow[\text{💡}]{\mathbf{2}\ (1\ \mu mol)} CH_3{}^{13}CO_2H + CH_3OH + {}^{13}CO_2$$

CH_4 5 bar; ^{13}CO 20 bar; air 1 bar

$CH_3{}^{13}CO_2H$: M+1: M > **20:1**; CH_3OH: no ^{13}C incorporation; $^{13}CO_2$: M+1 : M = **10:1**

C

$$CH_4 + CO + {}^{18}O_2/N_2 \xrightarrow[H_2O\ (500\ \mu L)]{\mathbf{2}\ (1\ \mu mol)} CH_3CO^{18}OH + CH_3{}^{18}OH + H_2{}^{18}O$$

CH_4 5 bar; CO 50 bar; $^{18}O_2/N_2$ 1 bar (1:4 ratio)

$CH_3CO^{18}OH$: M+2 : M = **1: 4.7**; $CH_3{}^{18}OH$: M+2 : M > **20: 1**; $H_2{}^{18}O$: M+2 : M = **1:8.6**

D

$$CH_4 + CO + air \xrightarrow[H_2{}^{18}O\ (500\ \mu L)]{\mathbf{2}\ (1\ \mu mol)} CH_3CO^{18}OH + CH_3OH + H_2{}^{18}O$$

CH_4 5 bar; CO 20 bar; air 1 bar

$CH_3CO^{18}OH$: M+2 : M = **2.7:1**; CH_3OH: no ^{18}O incorporation; $H_2{}^{18}O$: M+2 : M = **5:1**

E

$$CH_4 + CO + \mathbf{2} \xrightarrow[H_2{}^{18}O\ (300\ \mu L)]{\textit{without air}} CH_3CO^{18}OH + CH_3OH$$

CH_4 20 bar; CO 60 bar; **2** 0.4 mmol

$CH_3CO^{18}OH$: M+2 : M > **20:1**; CH_3OH: not detected

The proposed mechanism