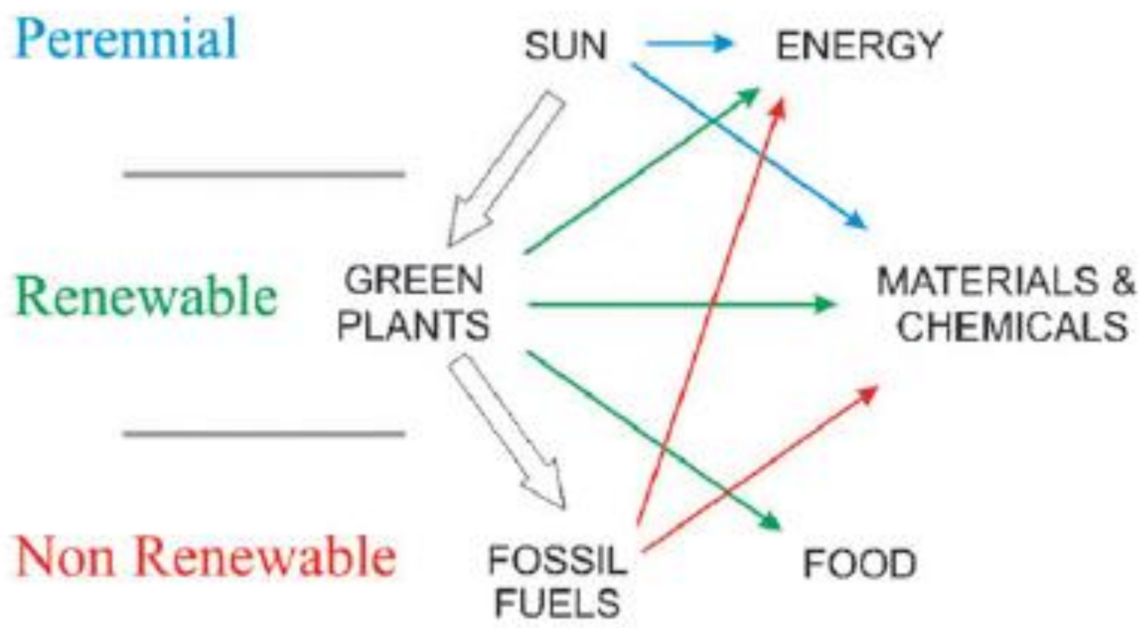
Fotocatalisi e sostenibilità

«…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 fist 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

Irradiazione Solare: 25000 – 75000 kWh per giorno per ettaro



Fotocatalisi e sostenibilità

Una reazione green deve:

- ✓ **Utilizzare in modo efficiente le fonti energetiche;**
- ✓ **Minimizzare la pericolosità relativa a reagenti e condizioni di reazione;**
- ✓ **Minimizzare i prodotti secondari;**
- ✓ **Usare fonti rinnovabili.**

Caratteristiche delle reazioni fotochimiche:

- ✓ **I fotoni come uno dei reagenti;**
- ✓ **Generazione di intermedi reattivi in condizioni blande;**
- ✓ **Alta selettività, bassi valori di E;**
- ✓ **Basse barriere energetiche;**
- ✓ **Versatilità nelle condizioni di reazioni.**

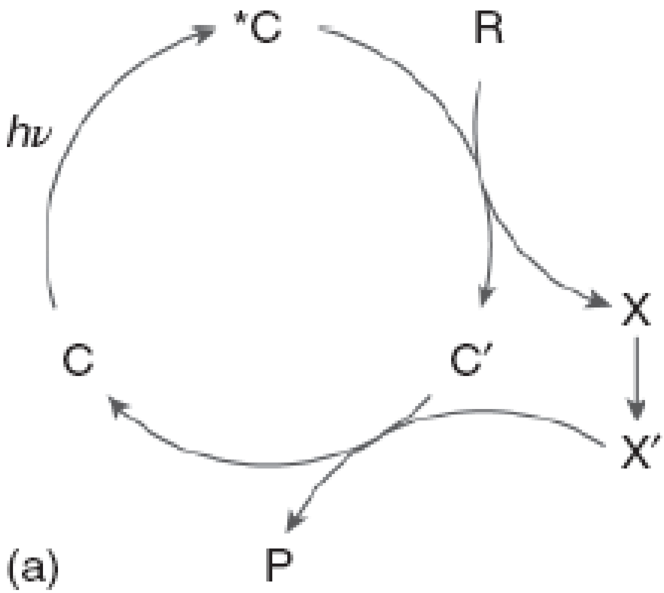
Limiti delle reazioni fotochimiche:

- ✓ **Soluzioni diluite;**
- ✓ **La fonte di luce: Luce Solare *vs* Luce Visibile Artificiale.**

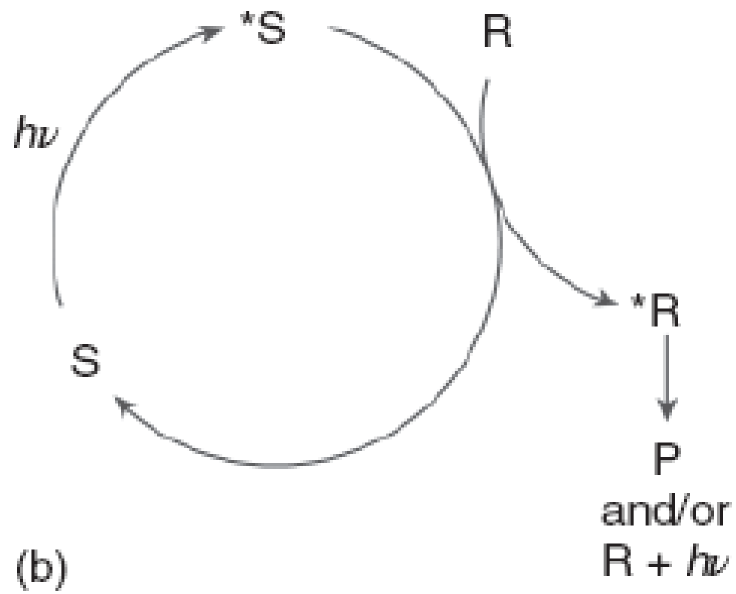
Fotocatalisi

Ogni reazione che richiede la presenza simultanea di un catalizzatore e di luce.

Fotocatalisi



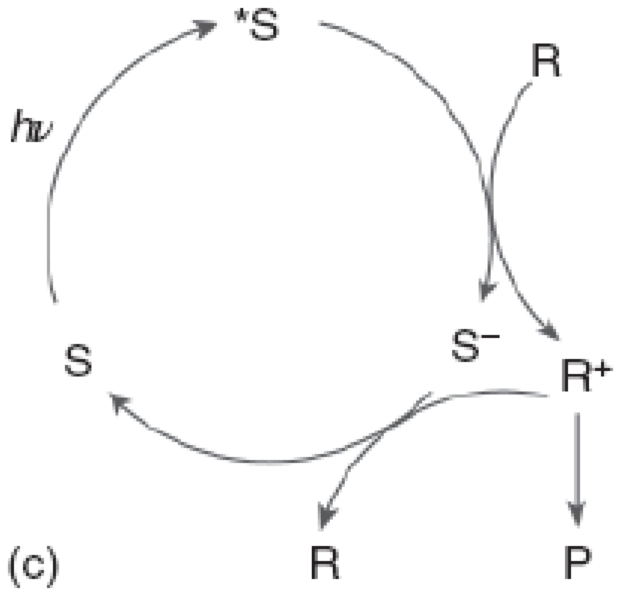
Energy-transfer photosensitization



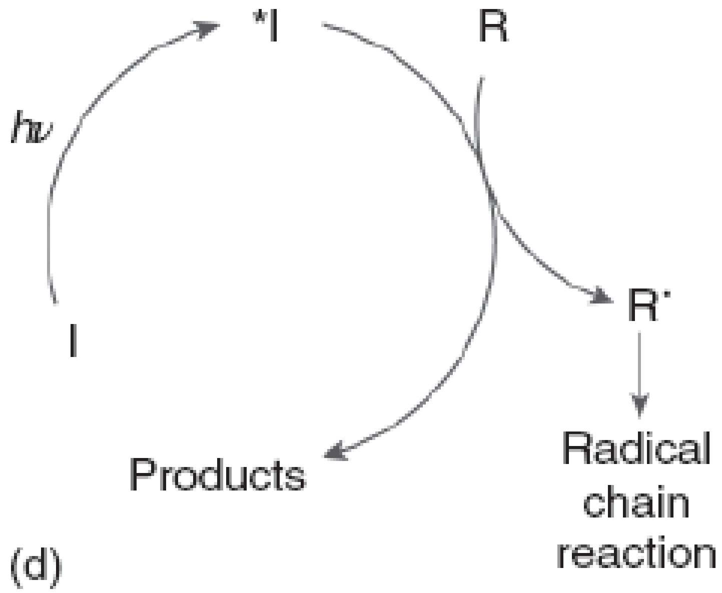
Fotocatalisi

Ogni reazione che richiede la presenza simultanea di un catalizzatore e di luce.

Electron-transfer photosensitization

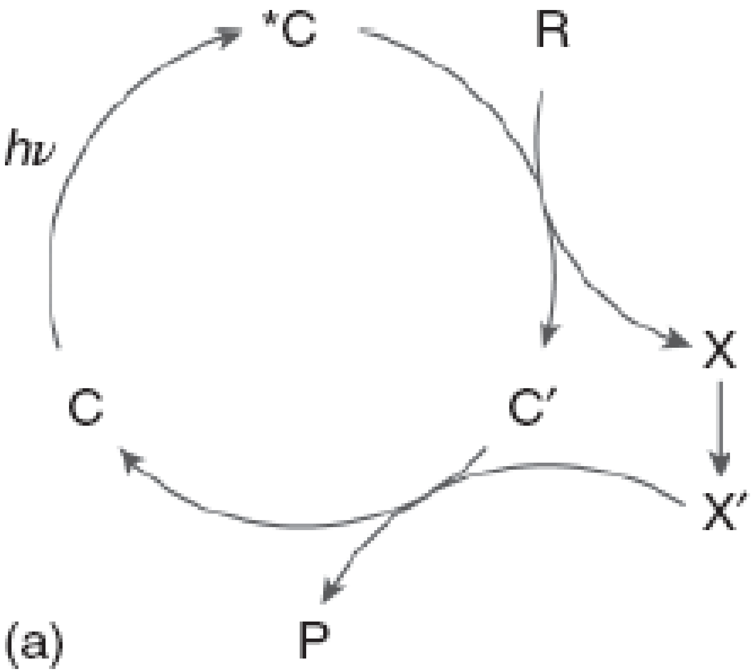


Photoinduced chain reaction



Fotocatalisi

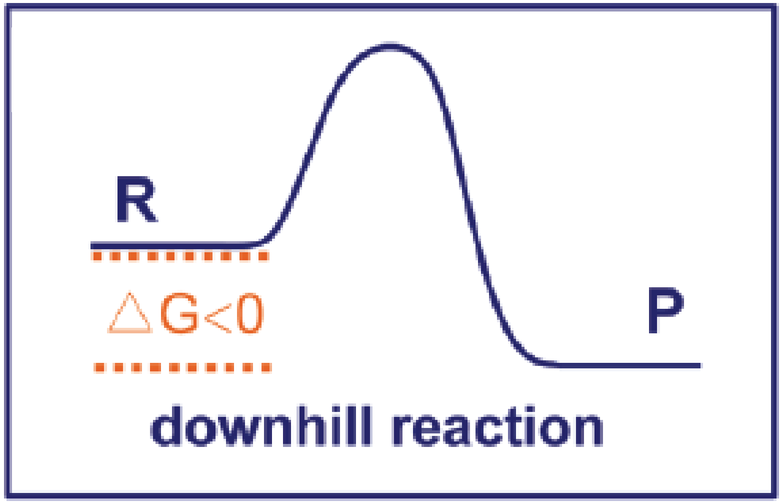
Ogni reazione che richiede la presenza simultanea di un catalizzatore e di luce.



(a)

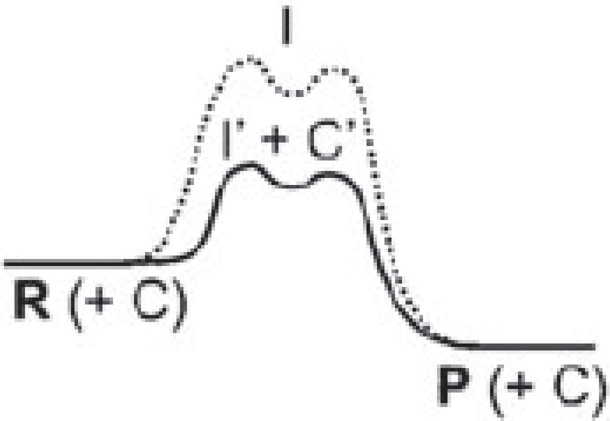
Fotocatalisi: aspetti termodinamici

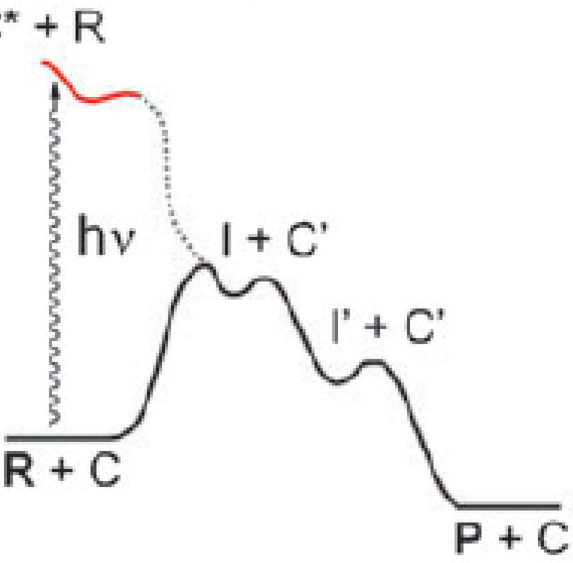
Reazioni spontanee



Reazione fotocatalitica

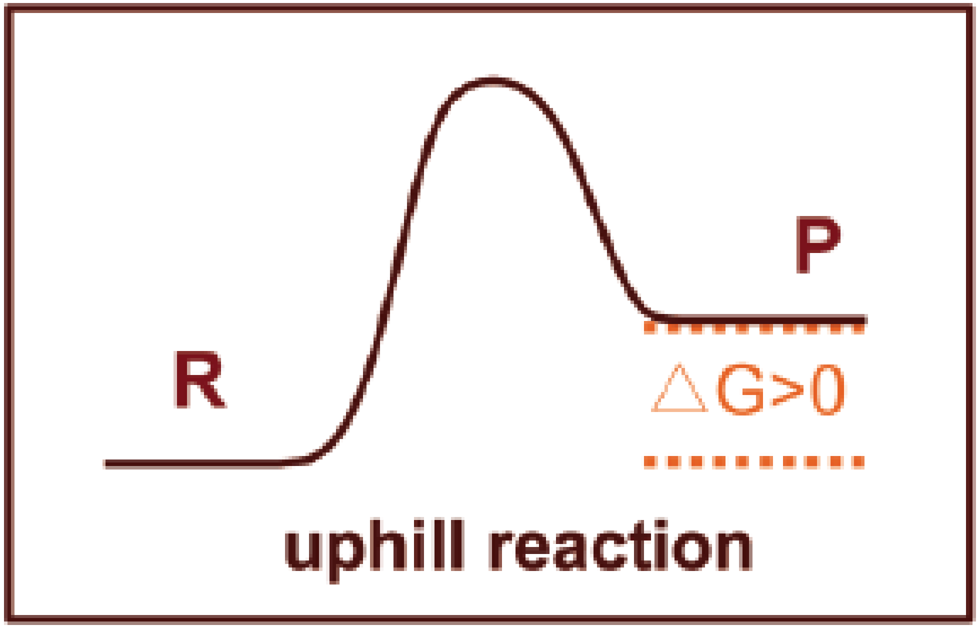
Reazione termica





Fotocatalisi: aspetti termodinamici

Reazioni NON spontanee

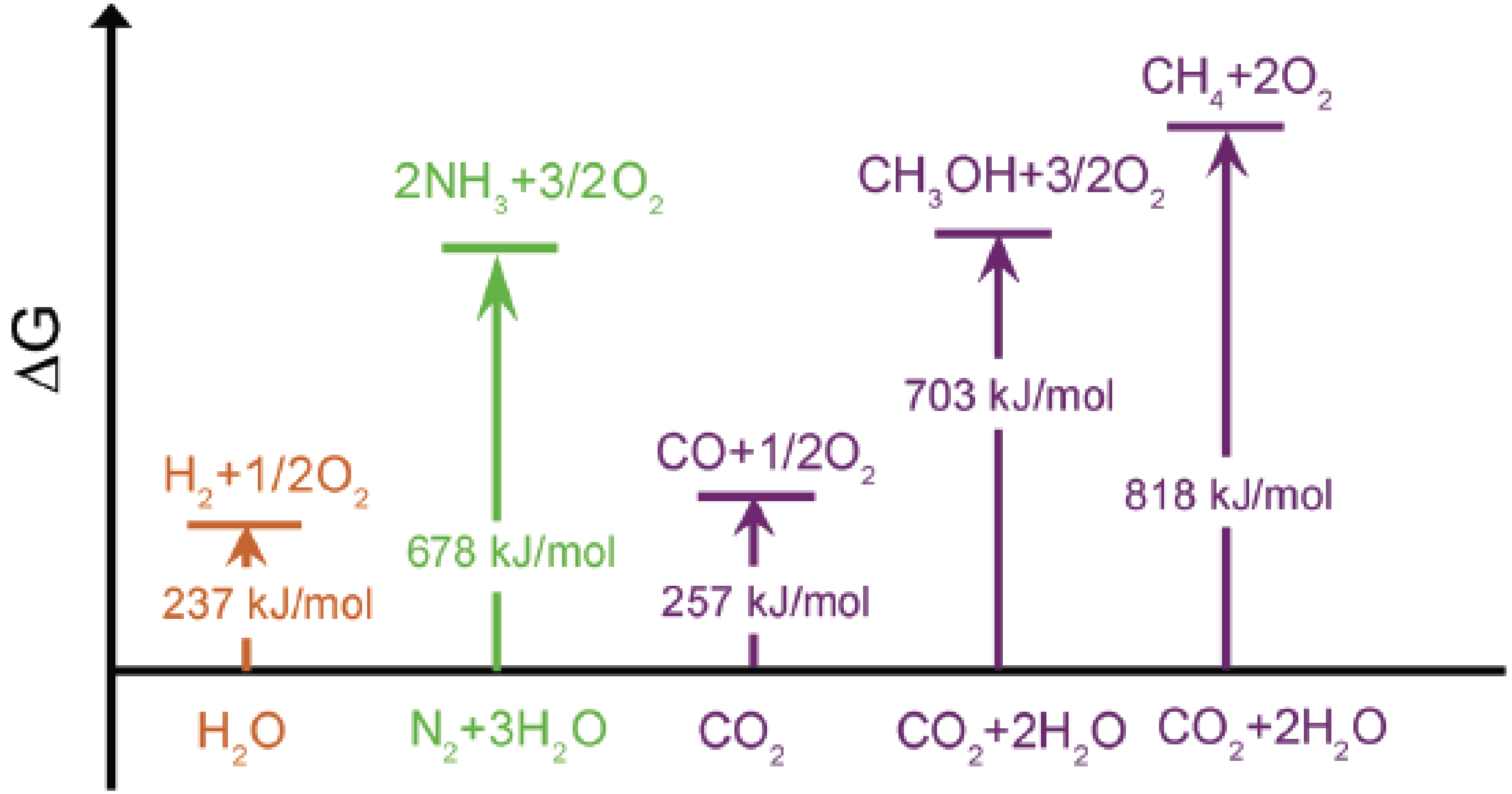


Significato più ampio

«.. 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.»

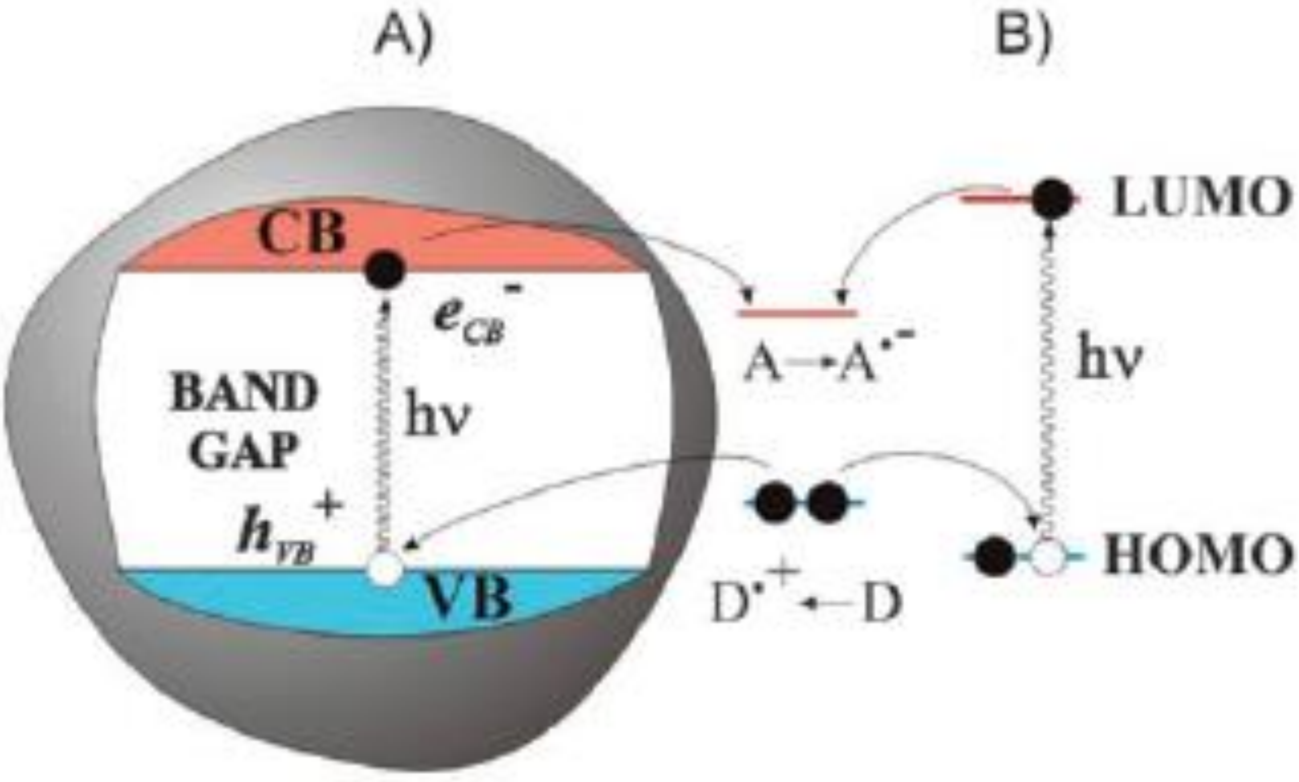
R. Noyori *Tetrahedron* 2010, *66*, 1028.

Reazioni uphill



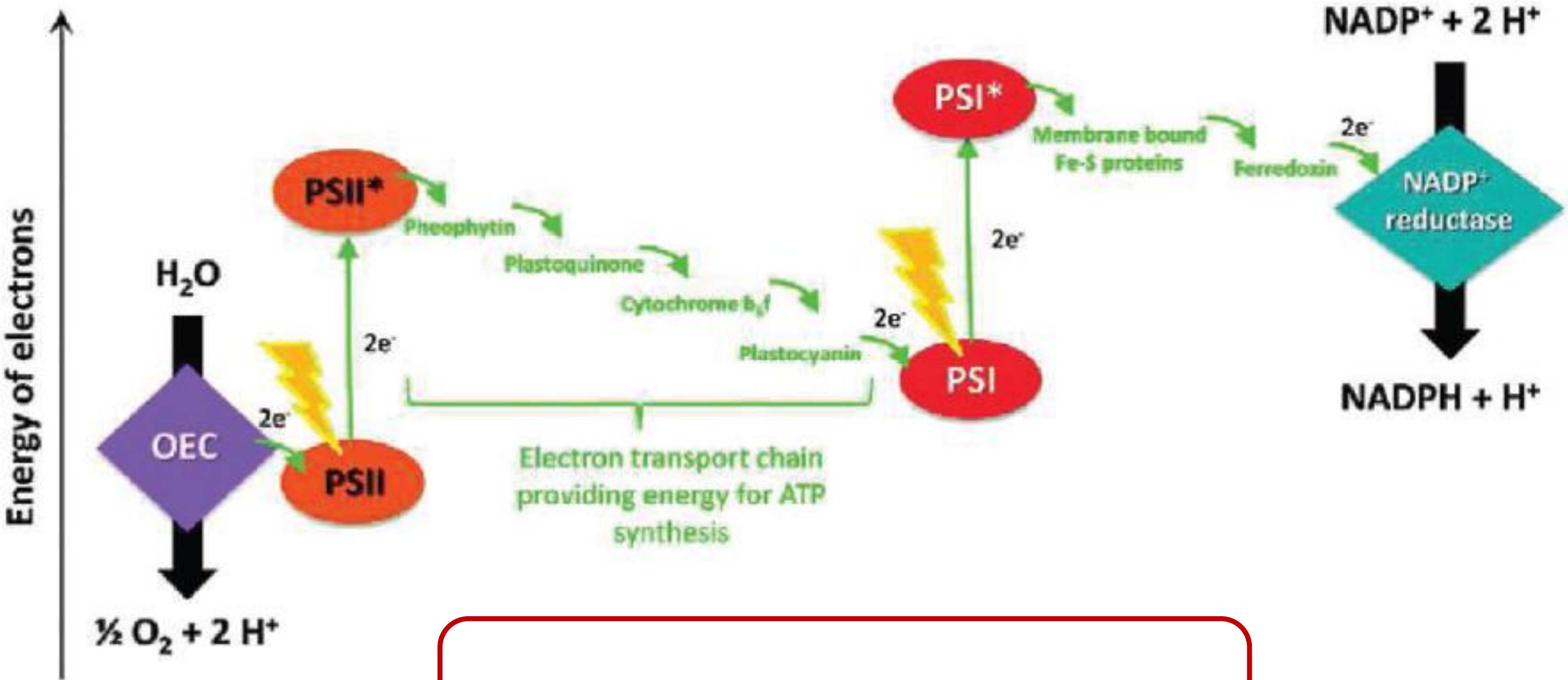
Stadi nei processi fotocatalitici

Fotocatalisi eterogenea **Fotocatalisi omogenea**



TON **TOF** **Φ**

Fotosintesi naturale



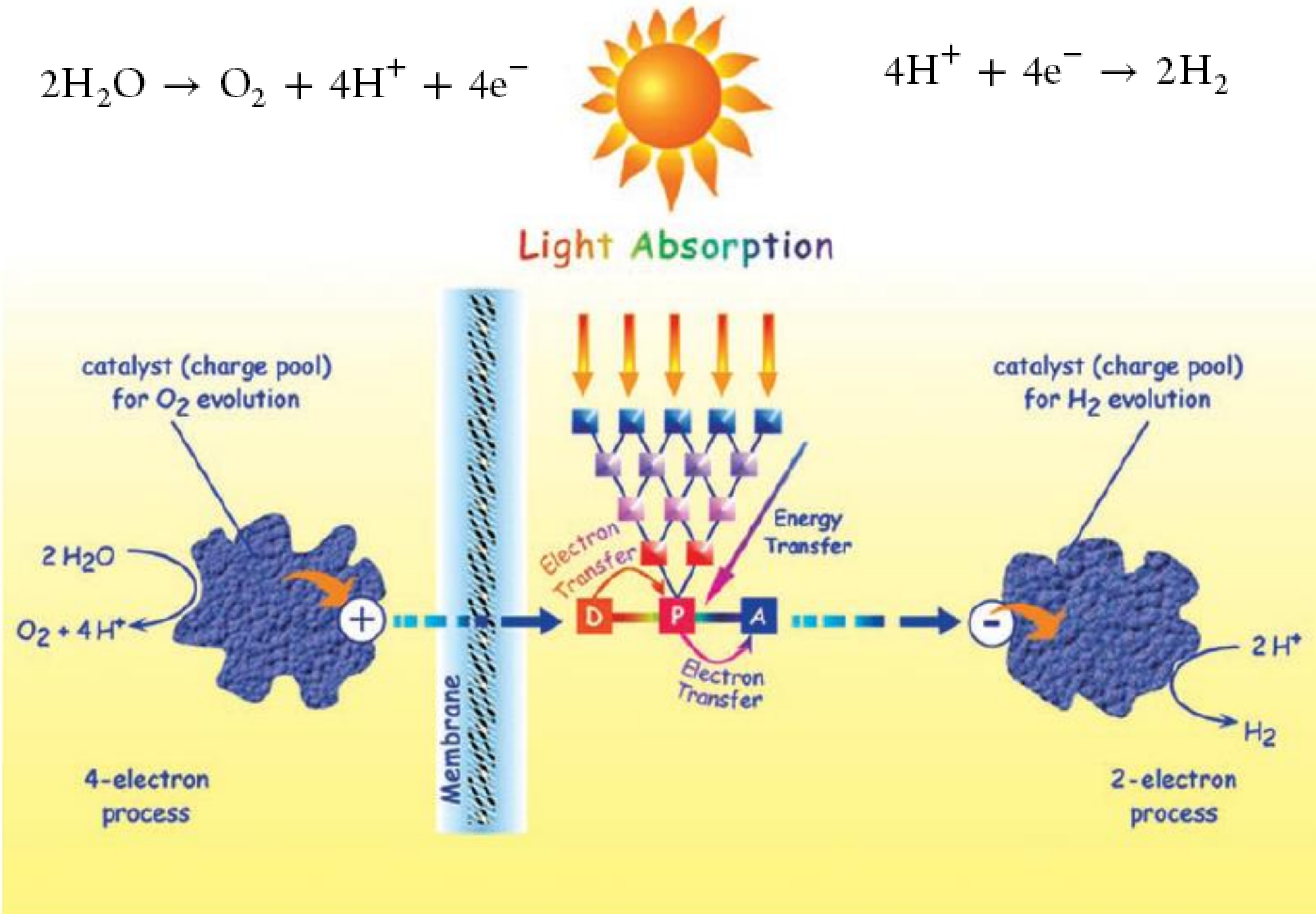
$$2H_2O + 4h\nu \rightarrow O_2 + 4H^+ + 4e^-$$

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

Fotosintesi artificiale

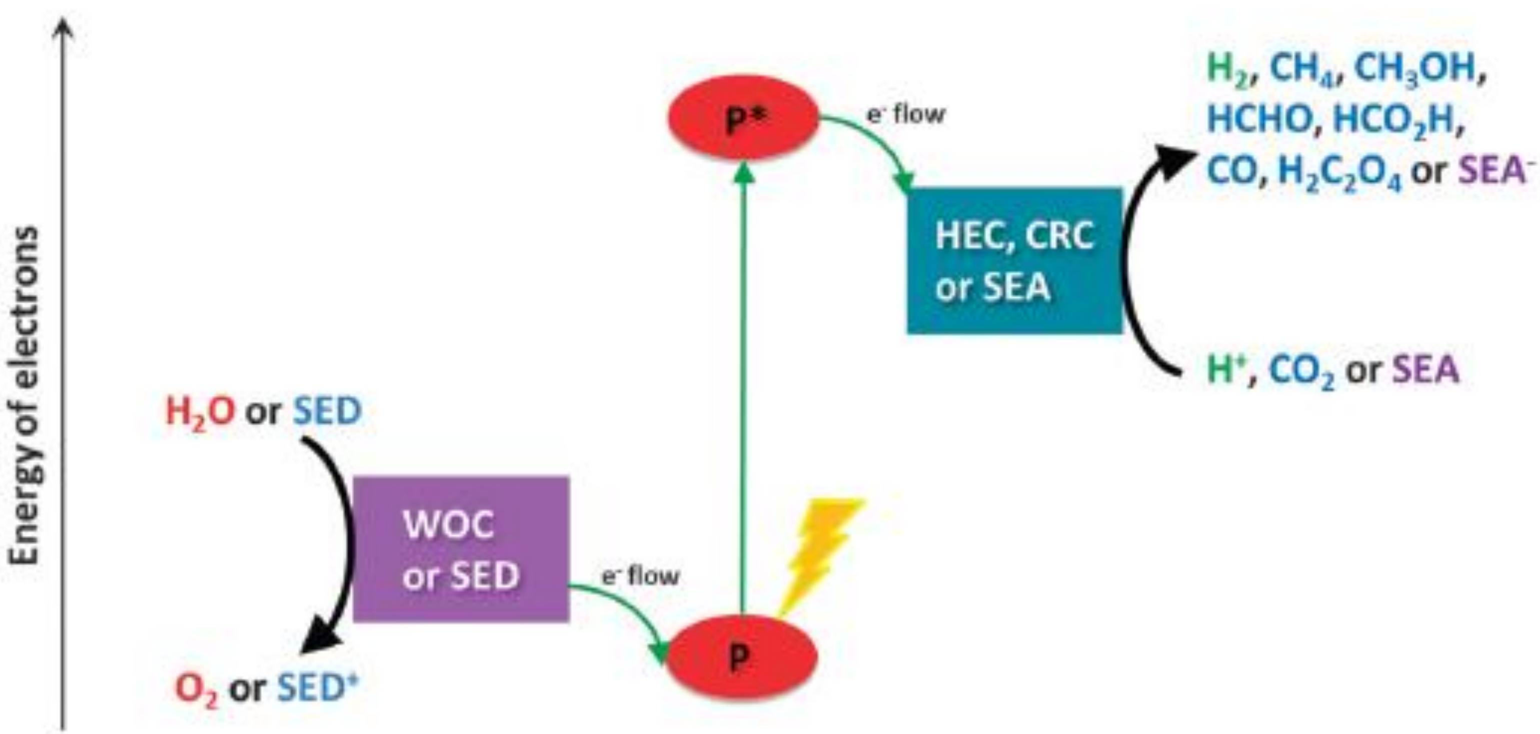
$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

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

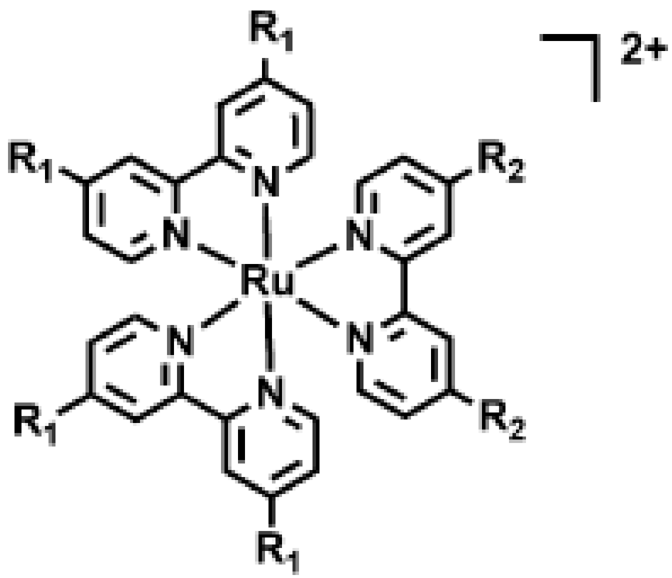


Fotosintesi artificiale

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

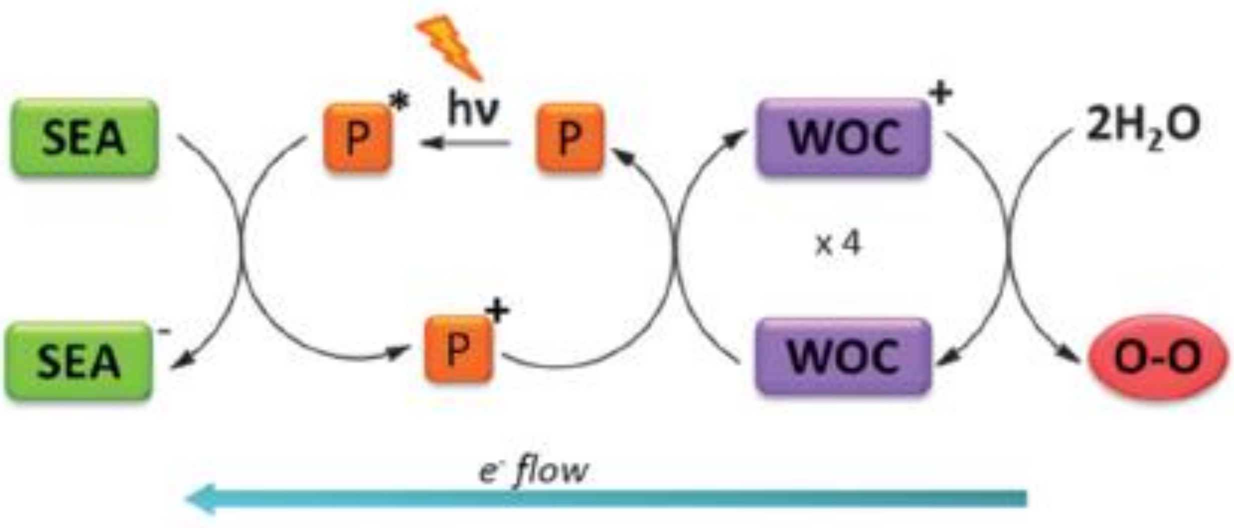


I fotosensibilizzatori



- 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

Miglior ossidante e miglior riducente per 2.12 V



Water oxidation catalysis

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

SEA più utilizzati

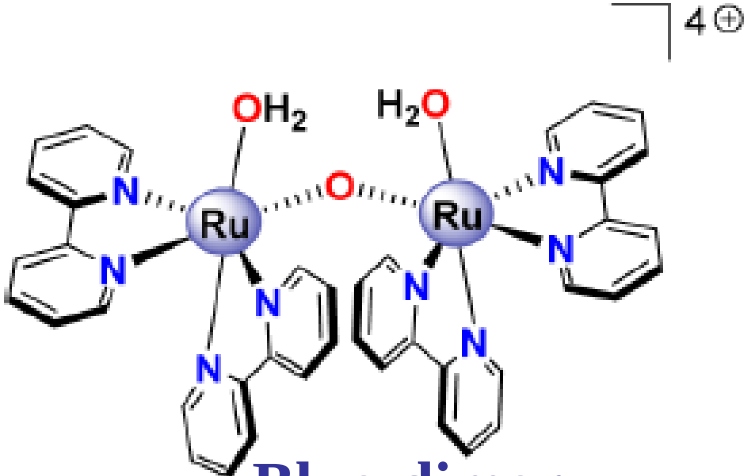
CAN $4Ce^{4+} + 4e^- \rightarrow 4Ce^{3+}$ $E^0 = 1.72\ V$

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

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

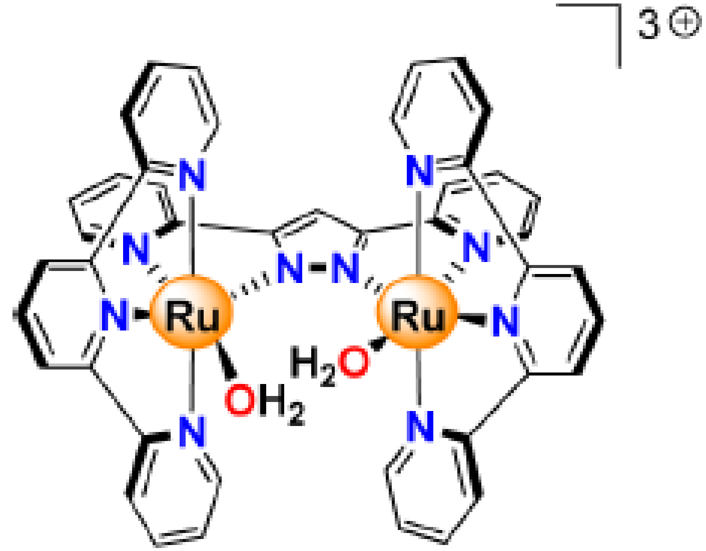
$$2H_2O + n\mathrm{Ox} \rightarrow 4H^+ + O_2 + n\mathrm{Red}$$

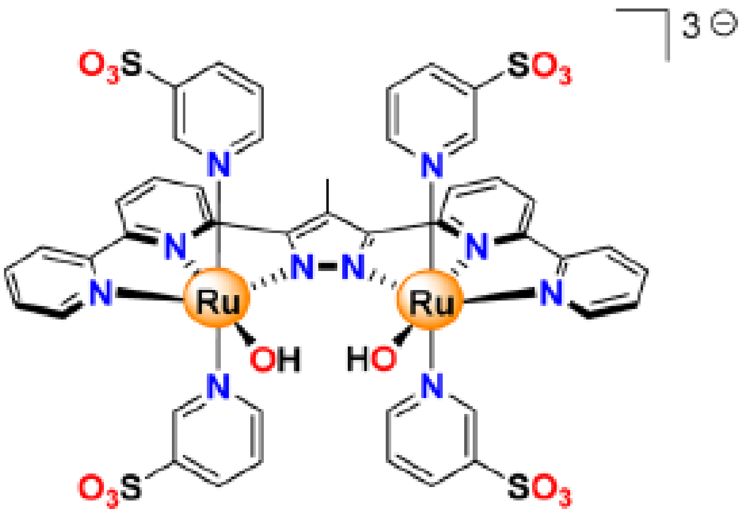
Ru-based Water Oxidation Catalysts

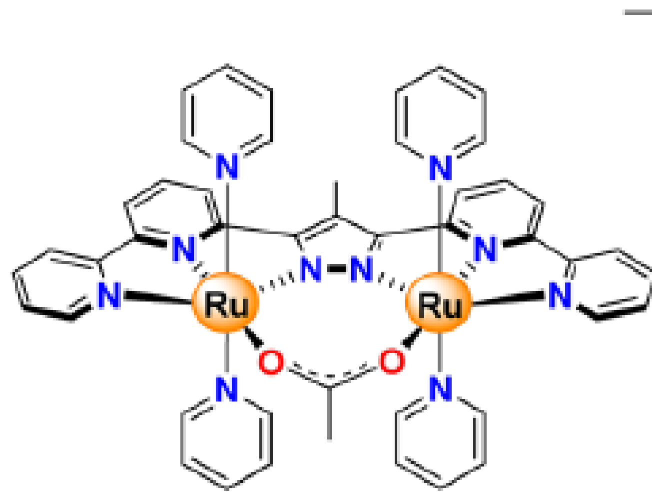


Blue-dimer

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



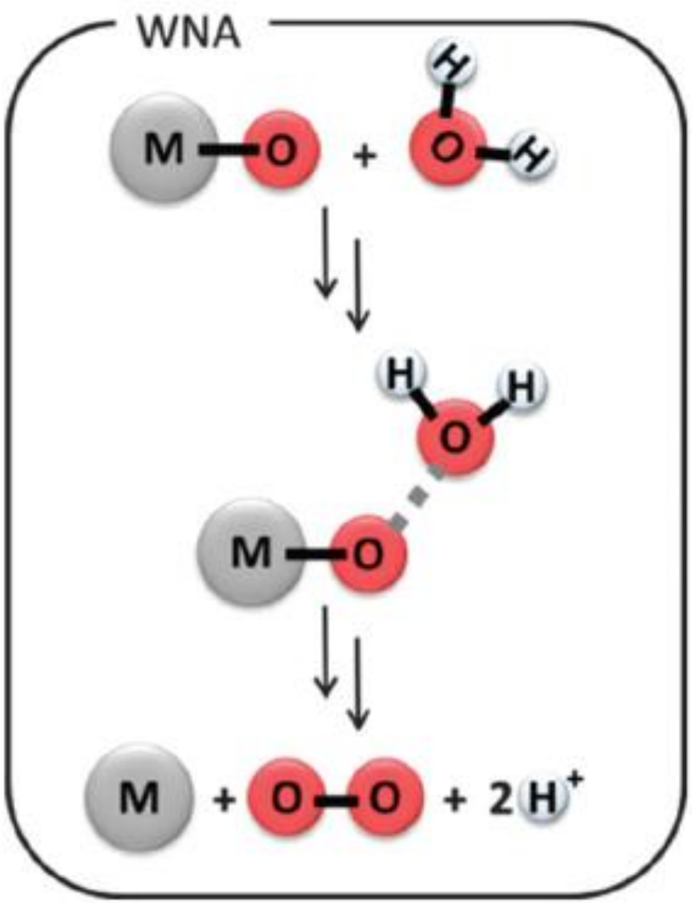


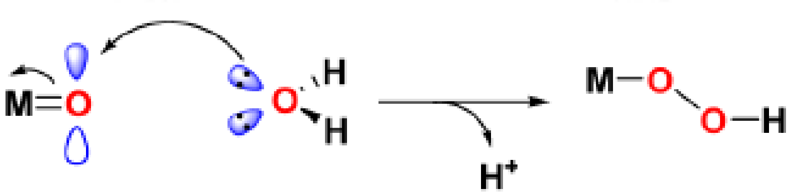


Akermark, B. et al., Chem. Rev. 2014, 114, 11863.

Possible mechanisms

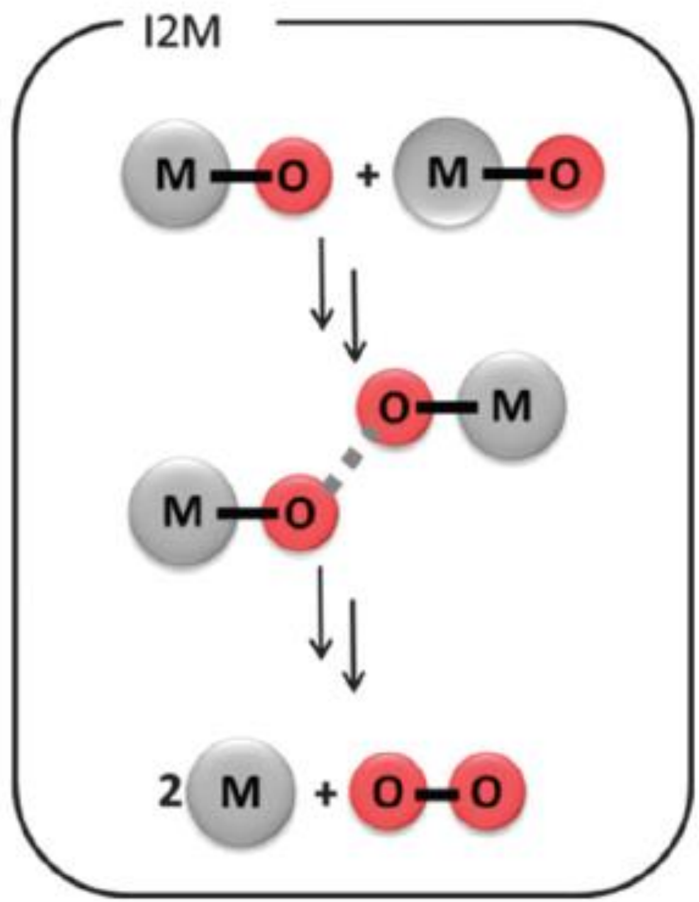
Water nucleophilic attack



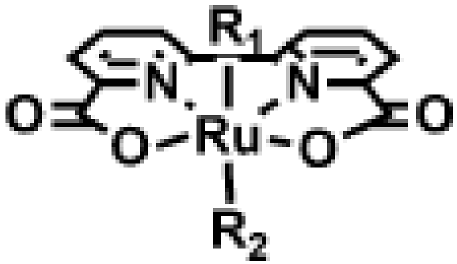


or

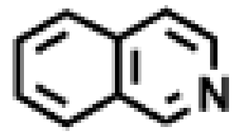
Interaction between two M-O units



Ru-based Water Oxidation Catalysts

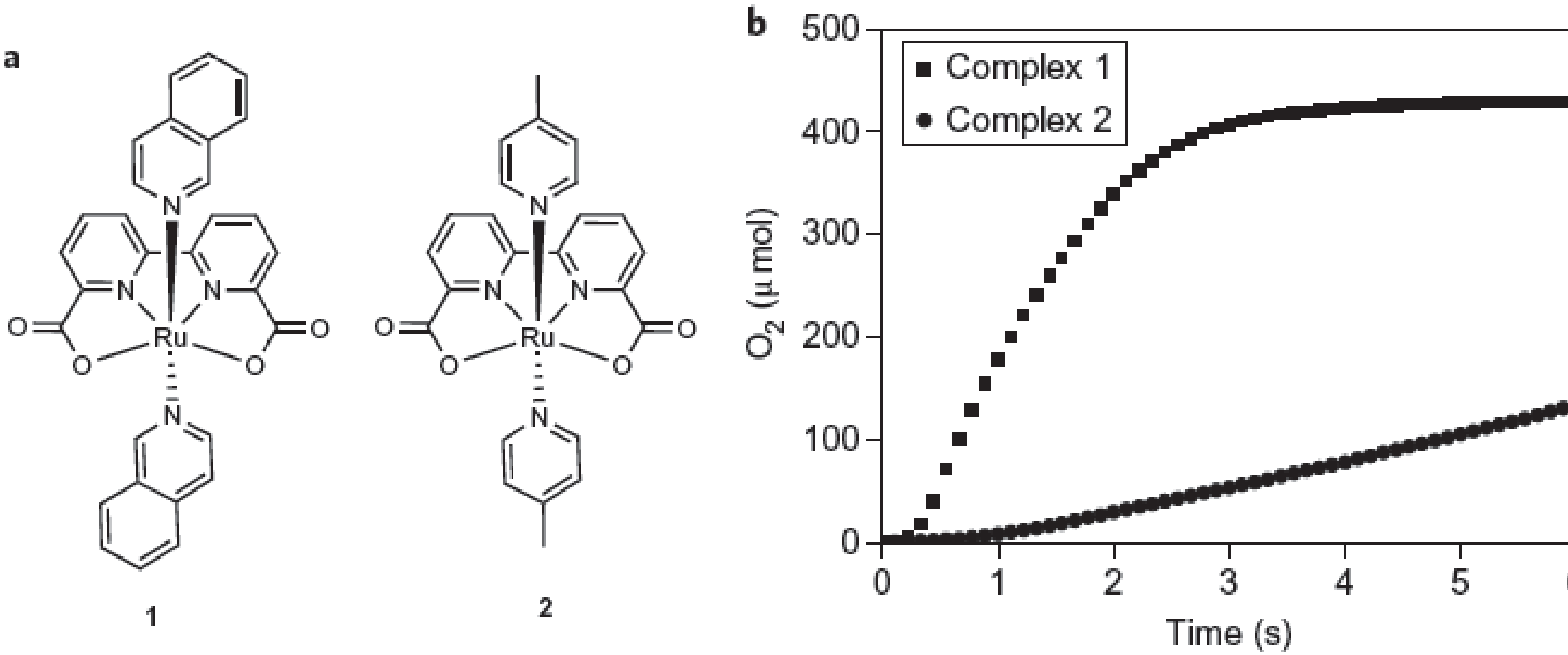


$R_1 = R_2 =$

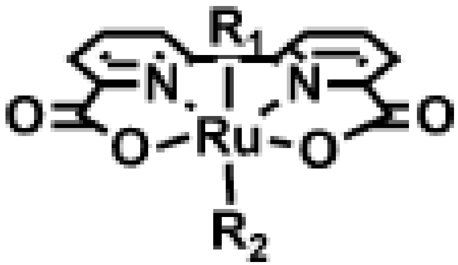


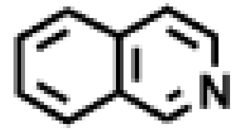
+ CAN [CAN]/[Ru] = 8000

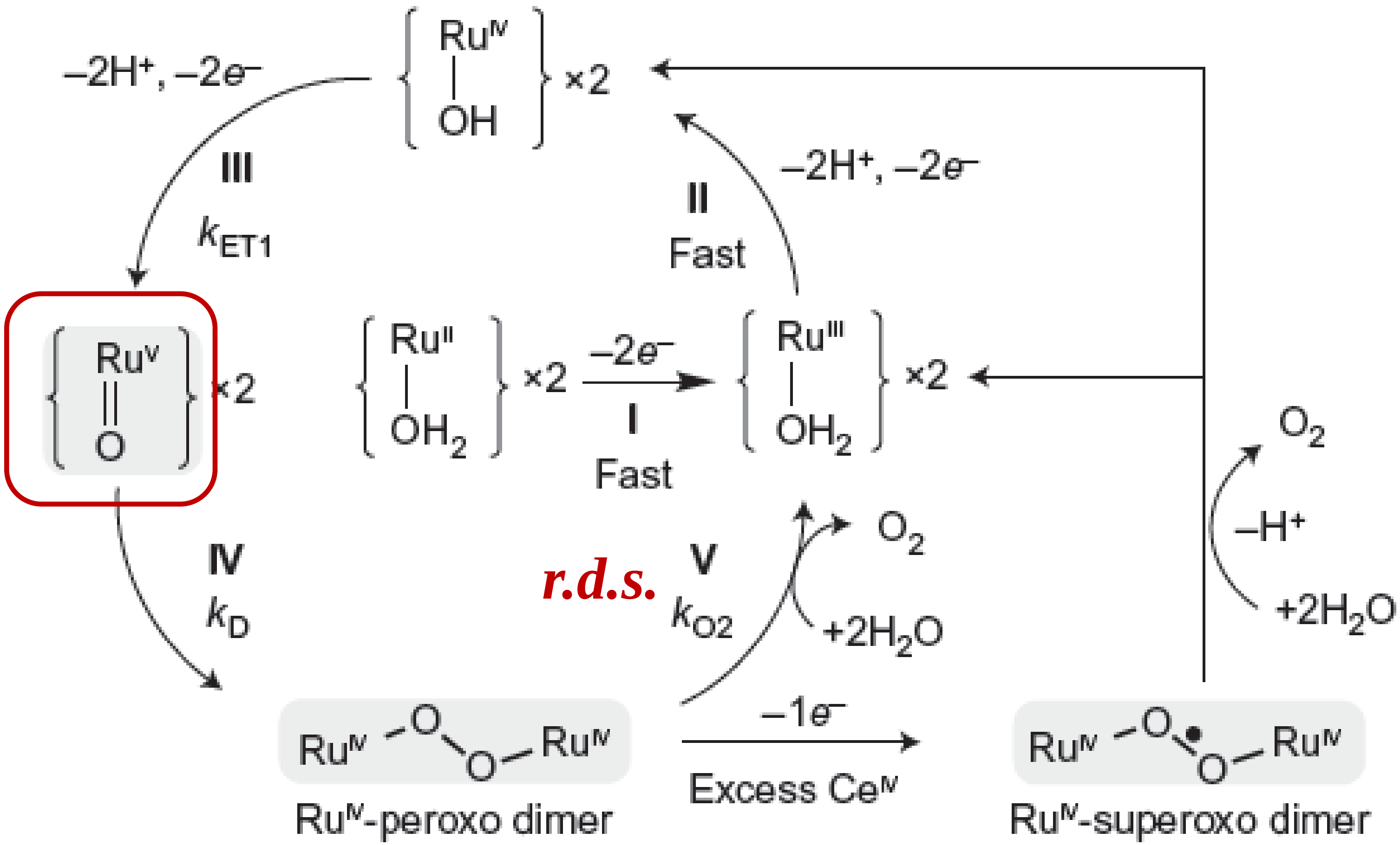
TON = $5.0 \cdot 10^4\ n_{O2}/n_{cat}$ TOF = 300 s^{-1}



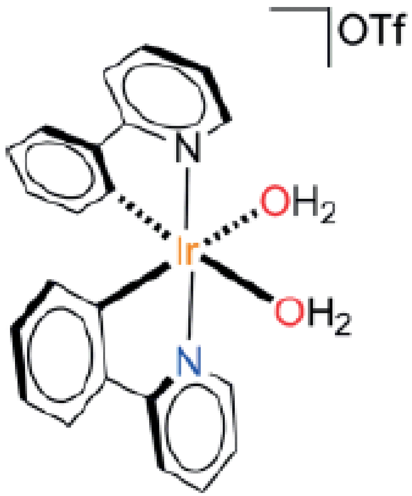
Possible mechanism



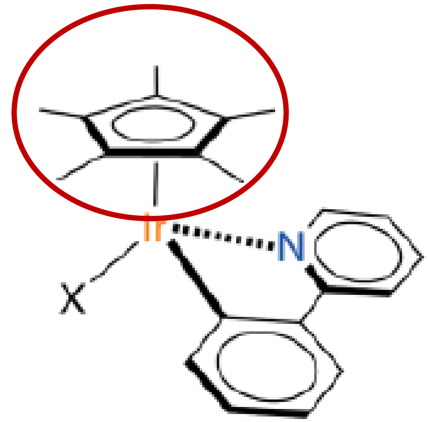
$R_1 = R_2 =$  **+ CAN [CAN]/[Ru] = 8000**



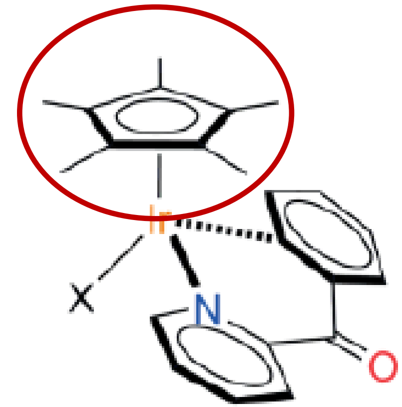
Ir-based Water Oxidation Catalysts



1, Bernhard 2008

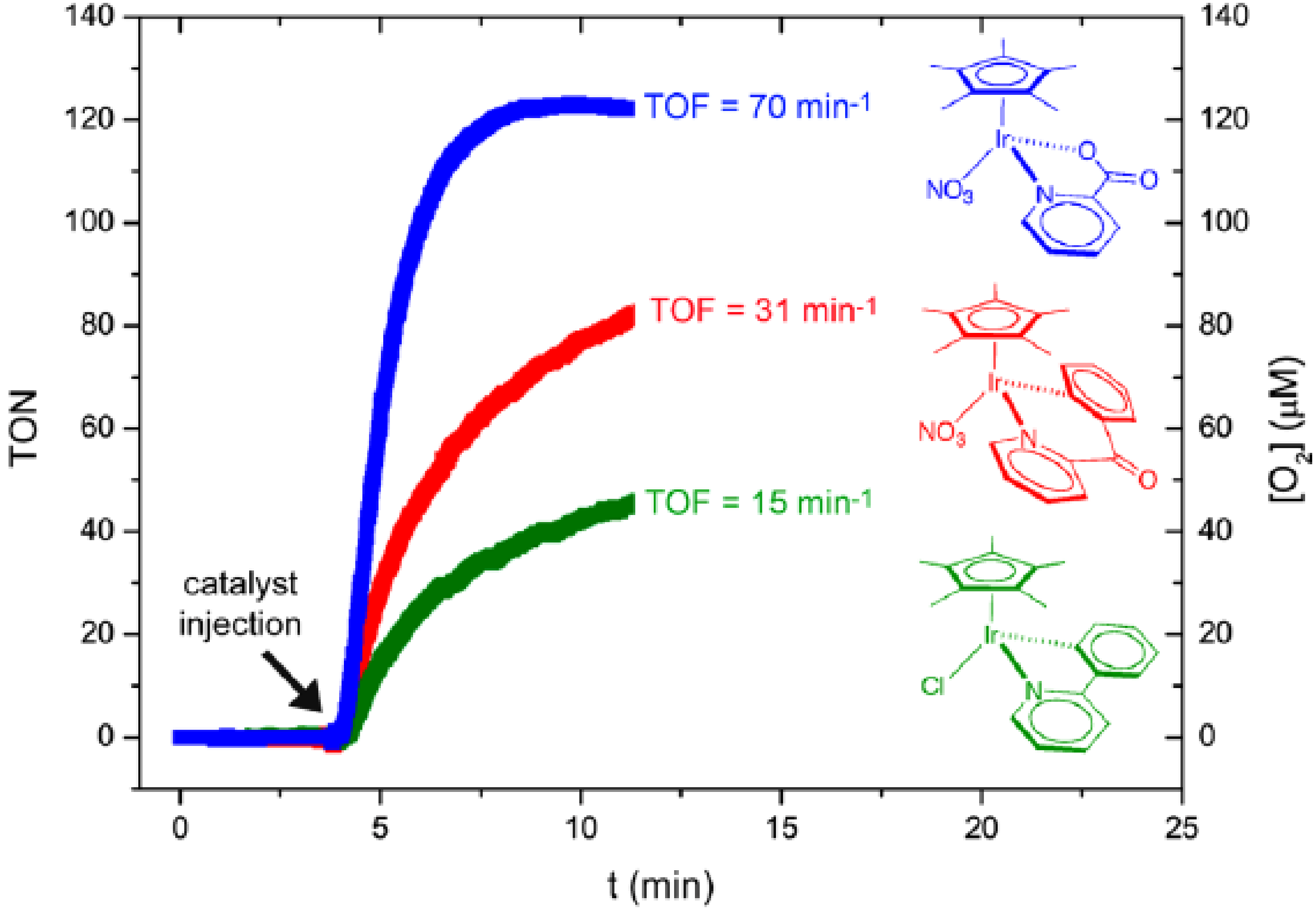


2, Crabtree 2009



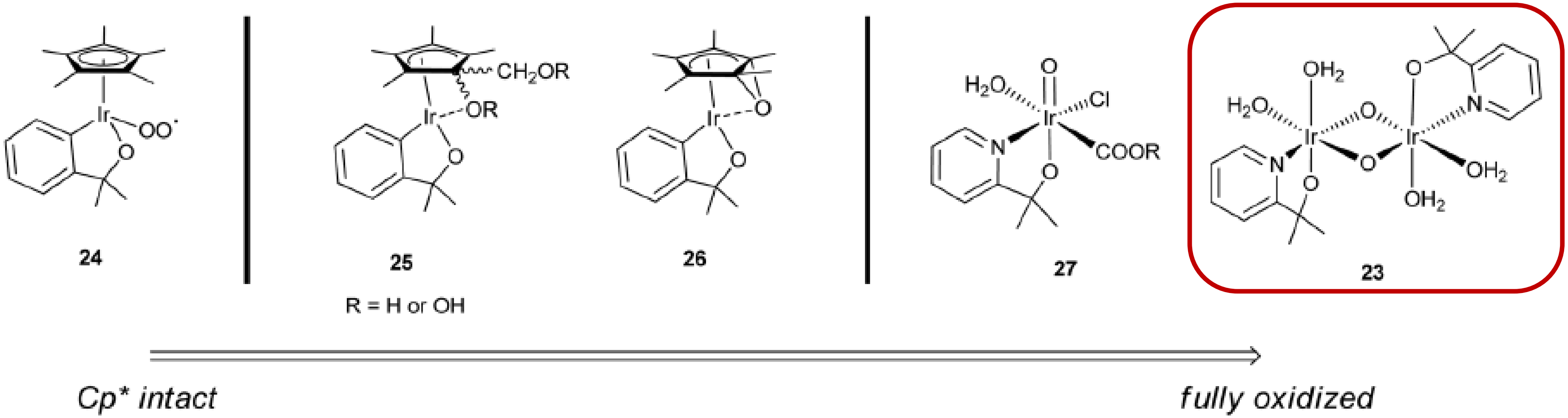
3, Macchioni 2010

Ir-based Water Oxidation Catalysts

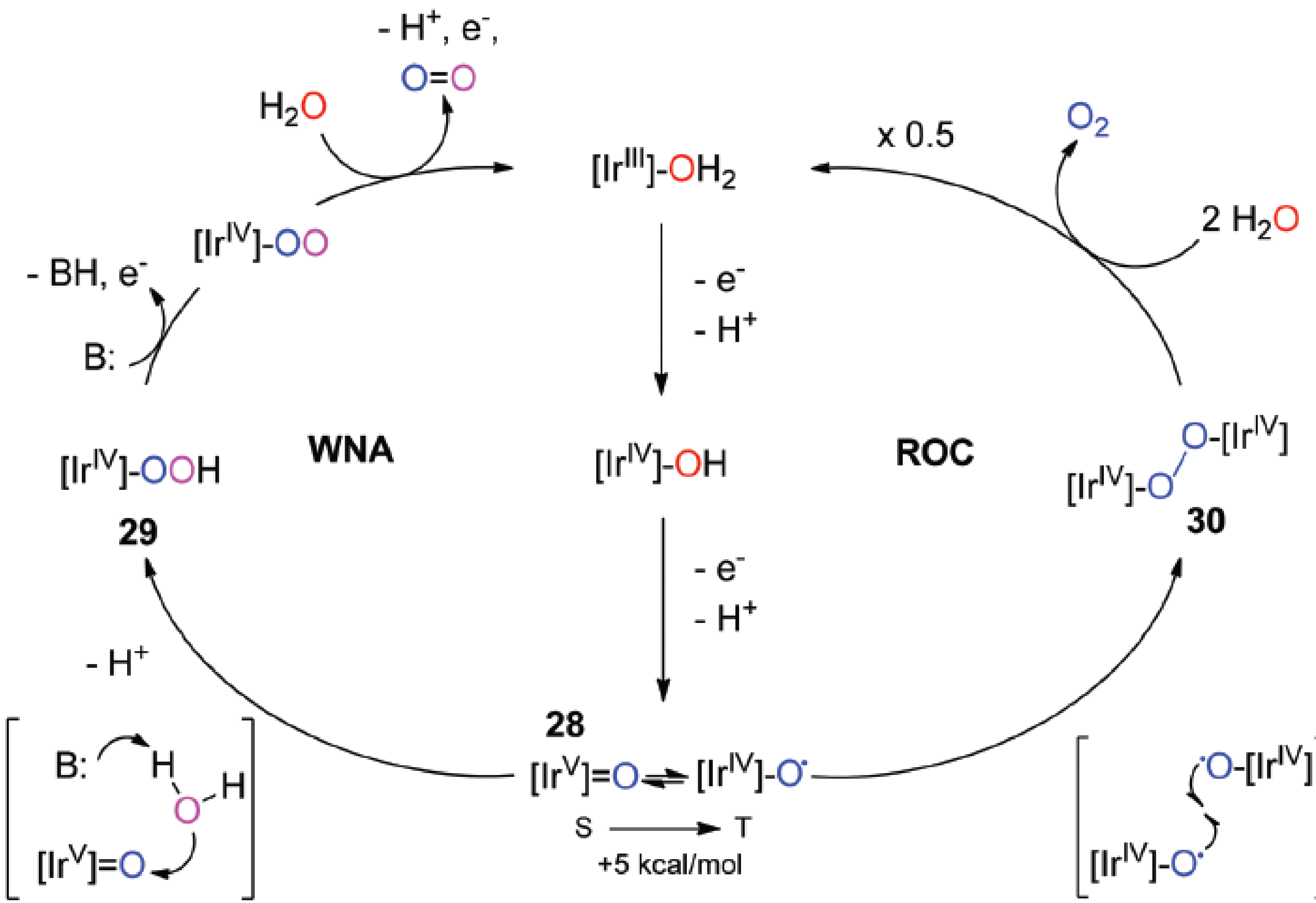


Condizioni di reazione: [CAN]/[Ir] = 40 000; pH = 1 per HNO_3; T = 25 °C; H_2O.

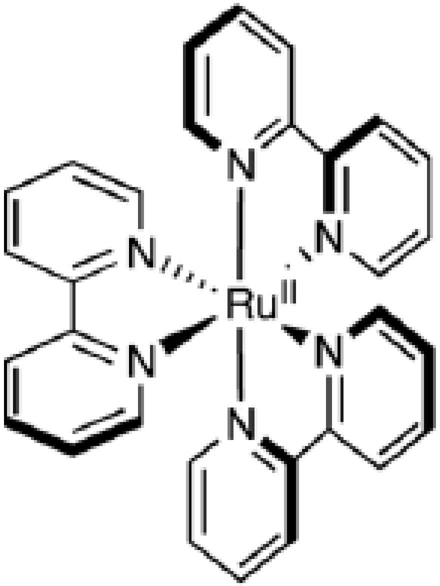
Possible mechanisms



Possible mechanisms



$[Ru(bpy)_3]^{2+}$: un catalizzatore fotoredox molto versatile



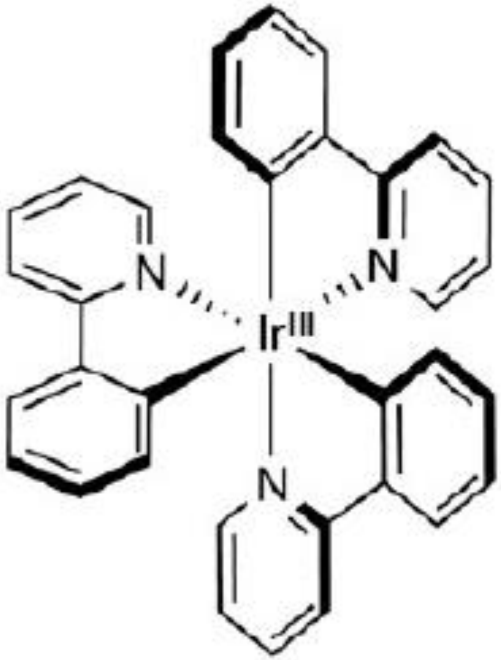
$Ru(bpy)_3^{2+}$

- 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 applicazioni in sintesi organica tra reazioni di riduzione, ossidazione, redox, e reazioni di energy transfer

[Ir(N-C)$_3$]: un catalizzatore fotoredox molto versatile

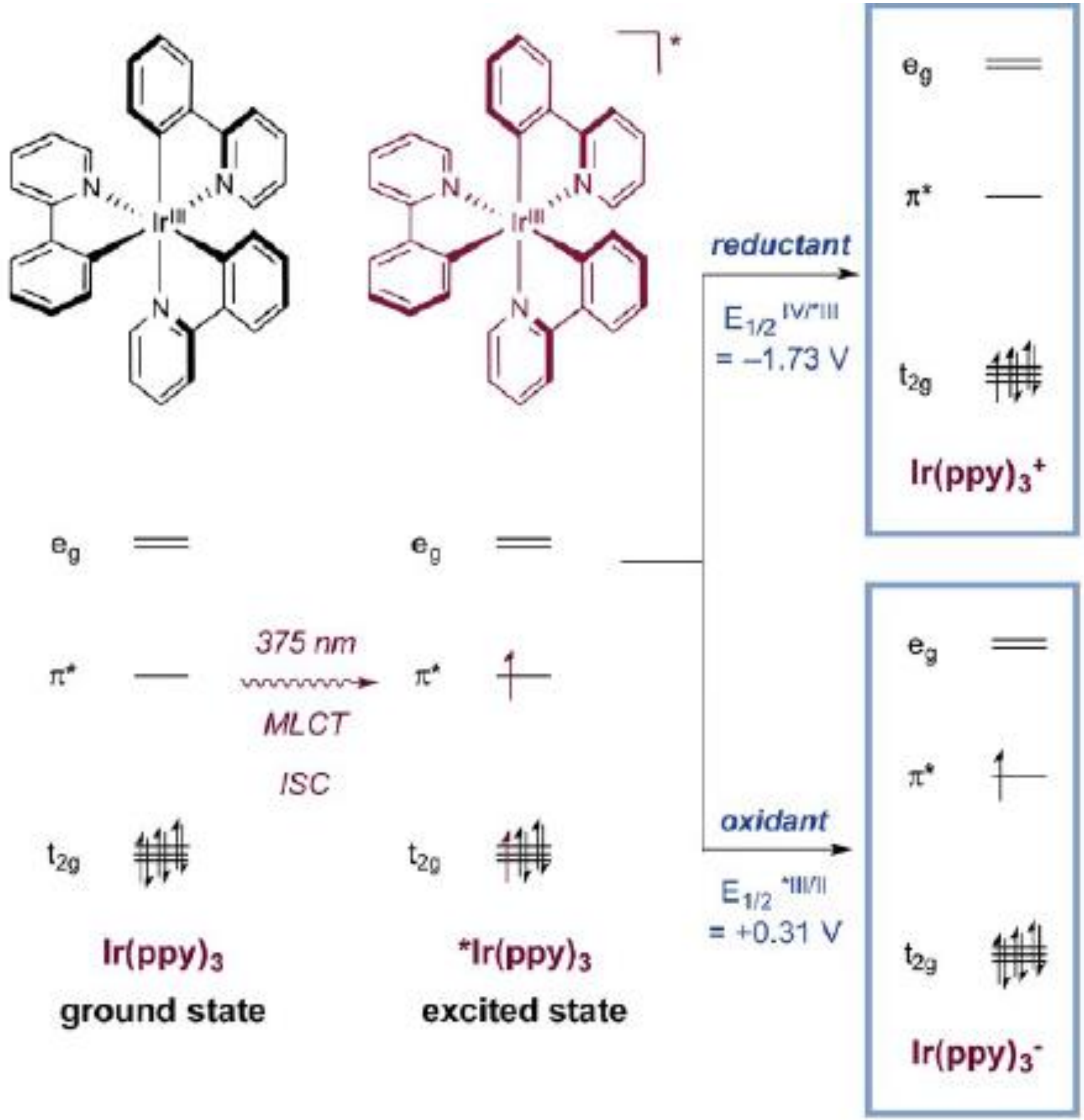


Ir(ppy)$_3$

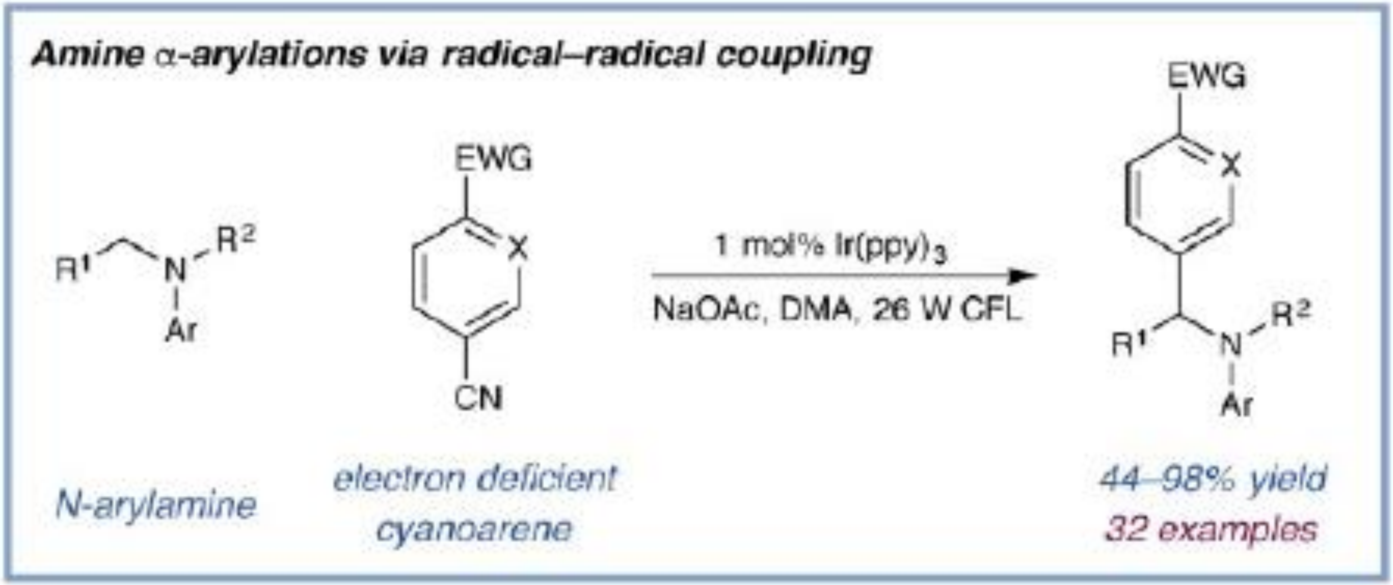
- Max absorption at 375 nm (visible light)
- Long-lived excited state ($\tau = 1.9\ \mu s$)
- Single-electron transfer catalyst
- Effective oxidant and reductant
- Triplet energy of 56 kcal mol^{-1}

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

$[Ir(N\text{-}C)_3]$: schema semplificato degli MO



Sintesi di amine con areni in alfa



Sintesi di amine con areni in alfa