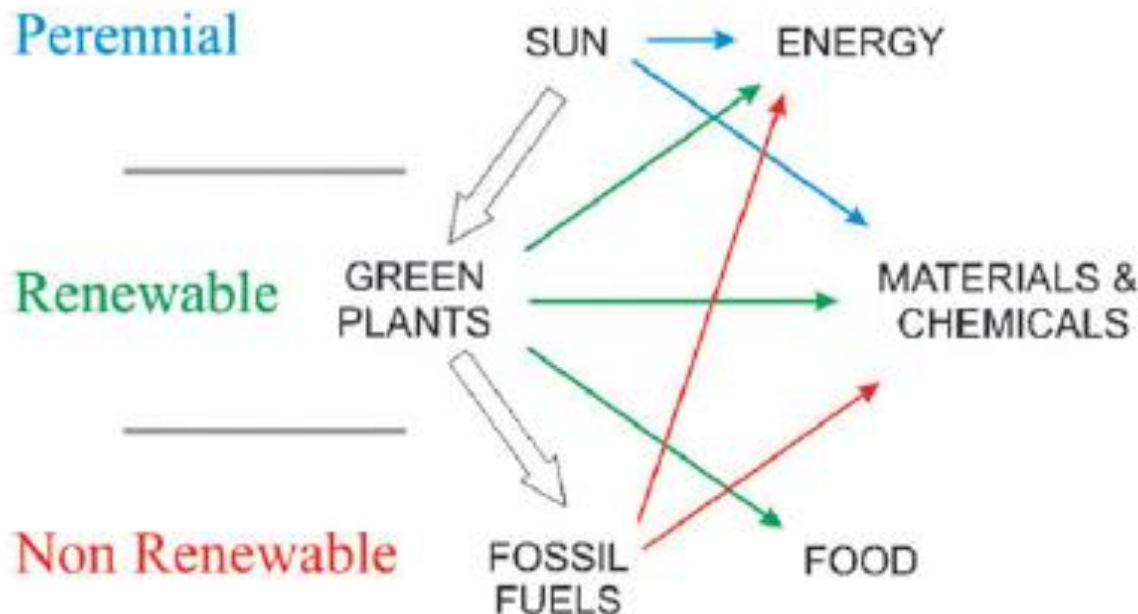


# Fotocatalisi e sostenibilità

«...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 using minimal means.... One should first consider **enzymes**... there is another agent of the highest importance for plants which deserves 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.

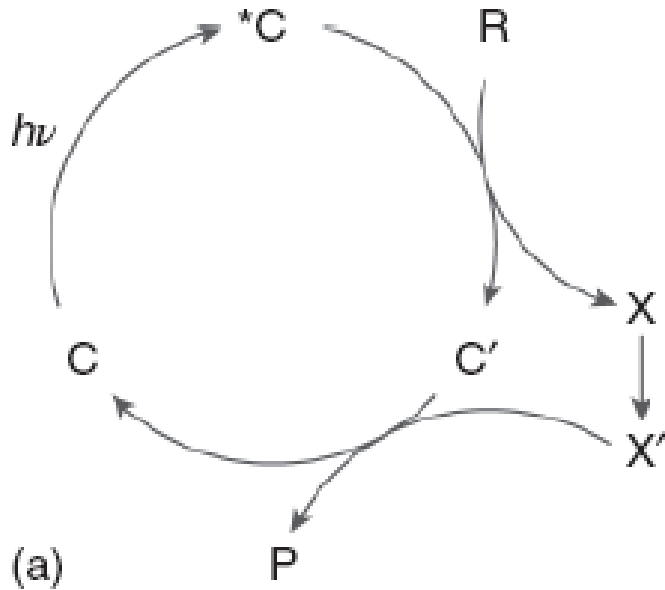
Limiti delle reazioni **fotochimiche**:

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

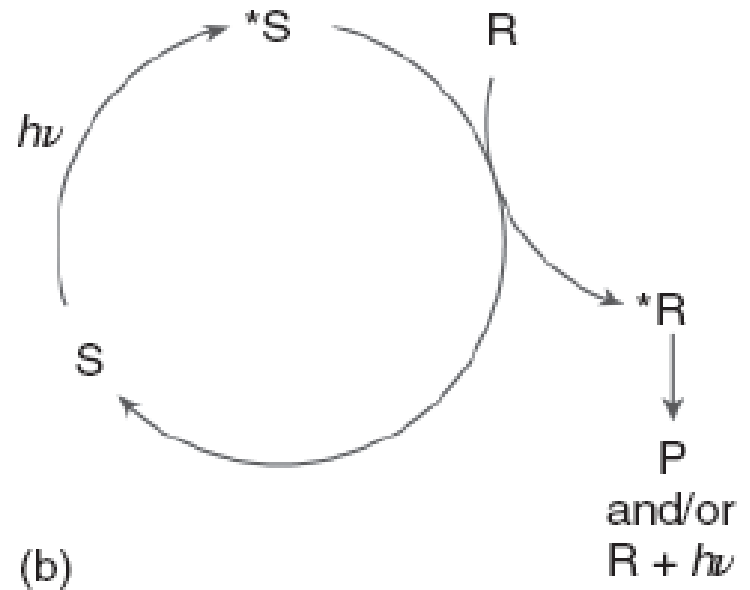
# Fotocatalisi

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

## Fotocatalisi



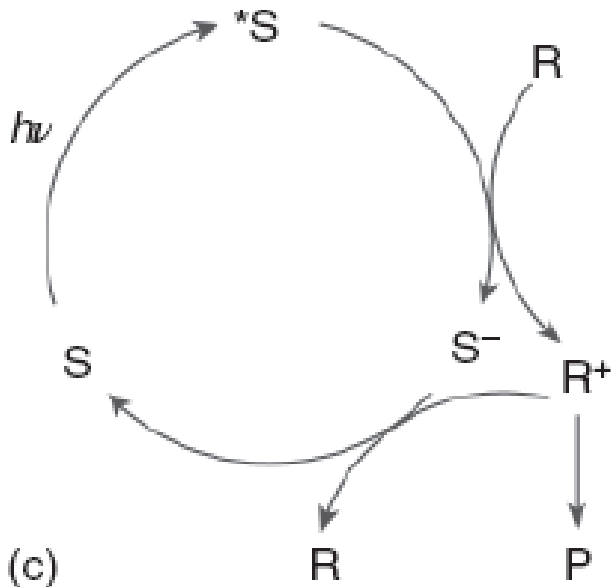
## Energy-transfer photosensitization



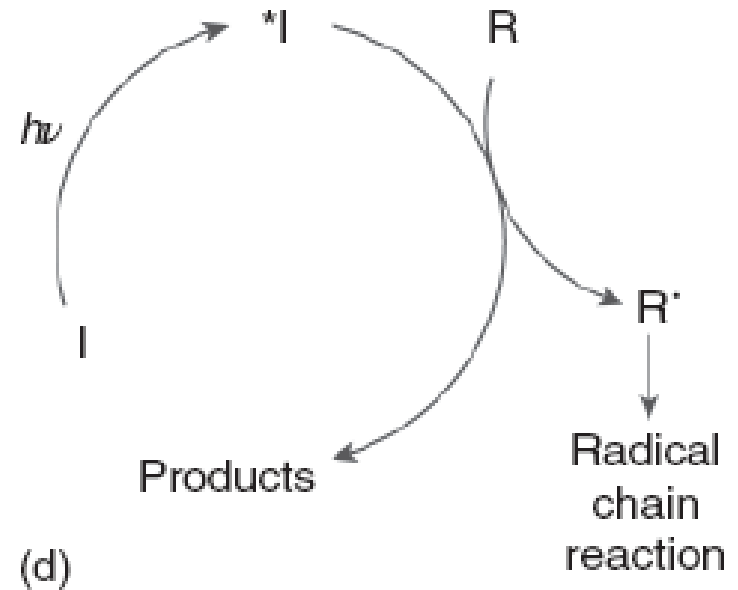
# Fotocatalisi

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

## Electron-transfer photosensitization

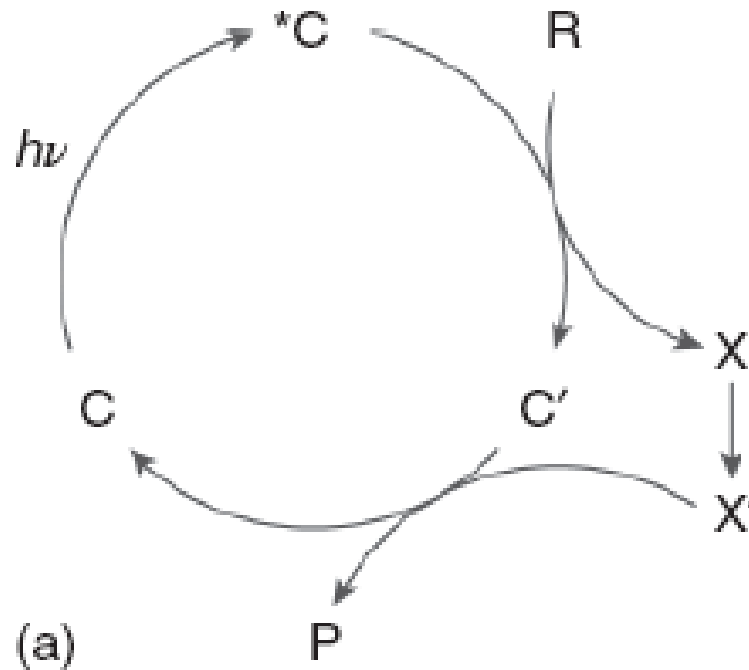


## Photoinduced chain reaction



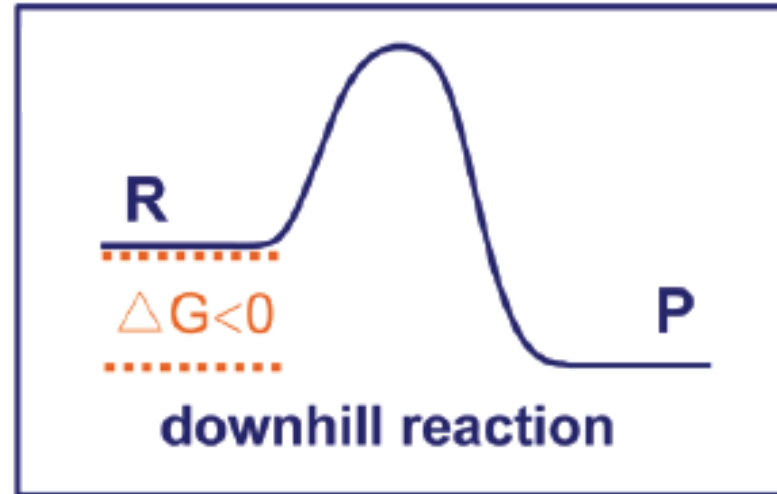
# Fotocatalisi

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



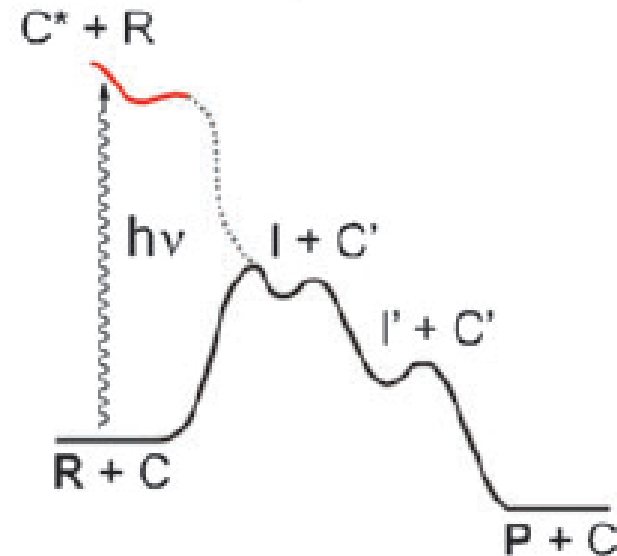
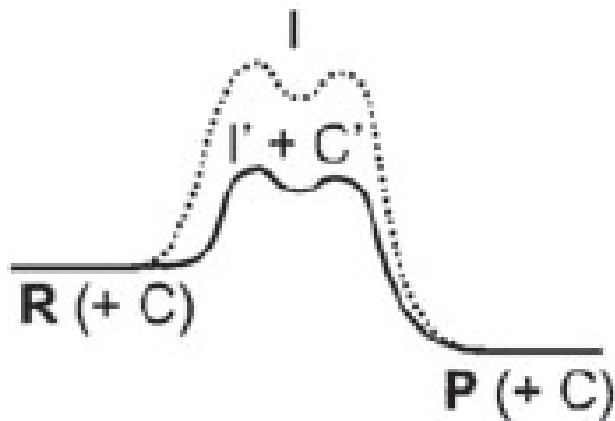
# Fotocatalisi: aspetti termodinamici

Reazioni **spontanee**



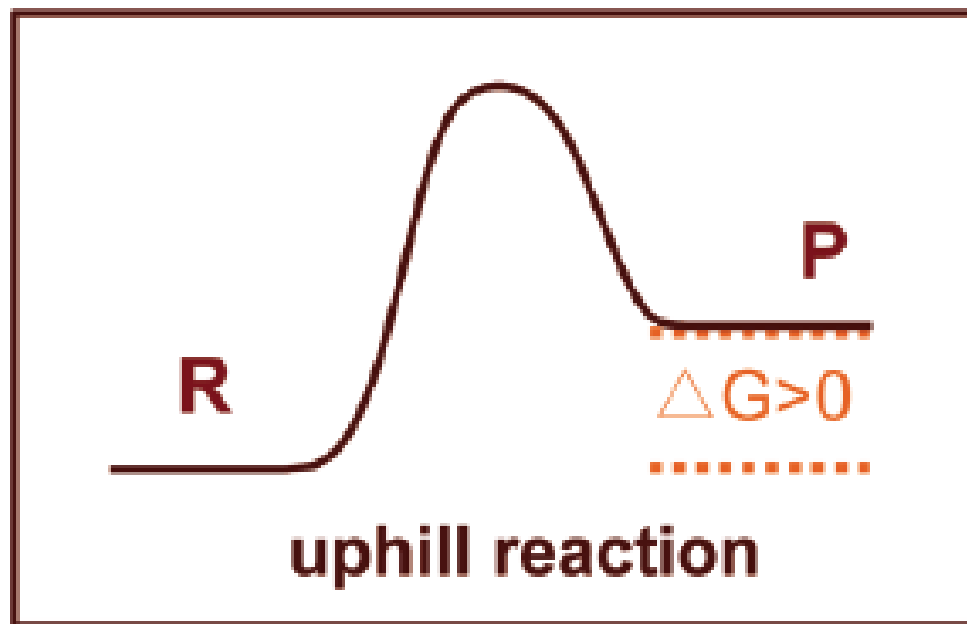
Reazione **fotocatalitica**

Reazione **termica**



# Fotocatalisi: aspetti termodinamici

Reazioni **NON** spontanee

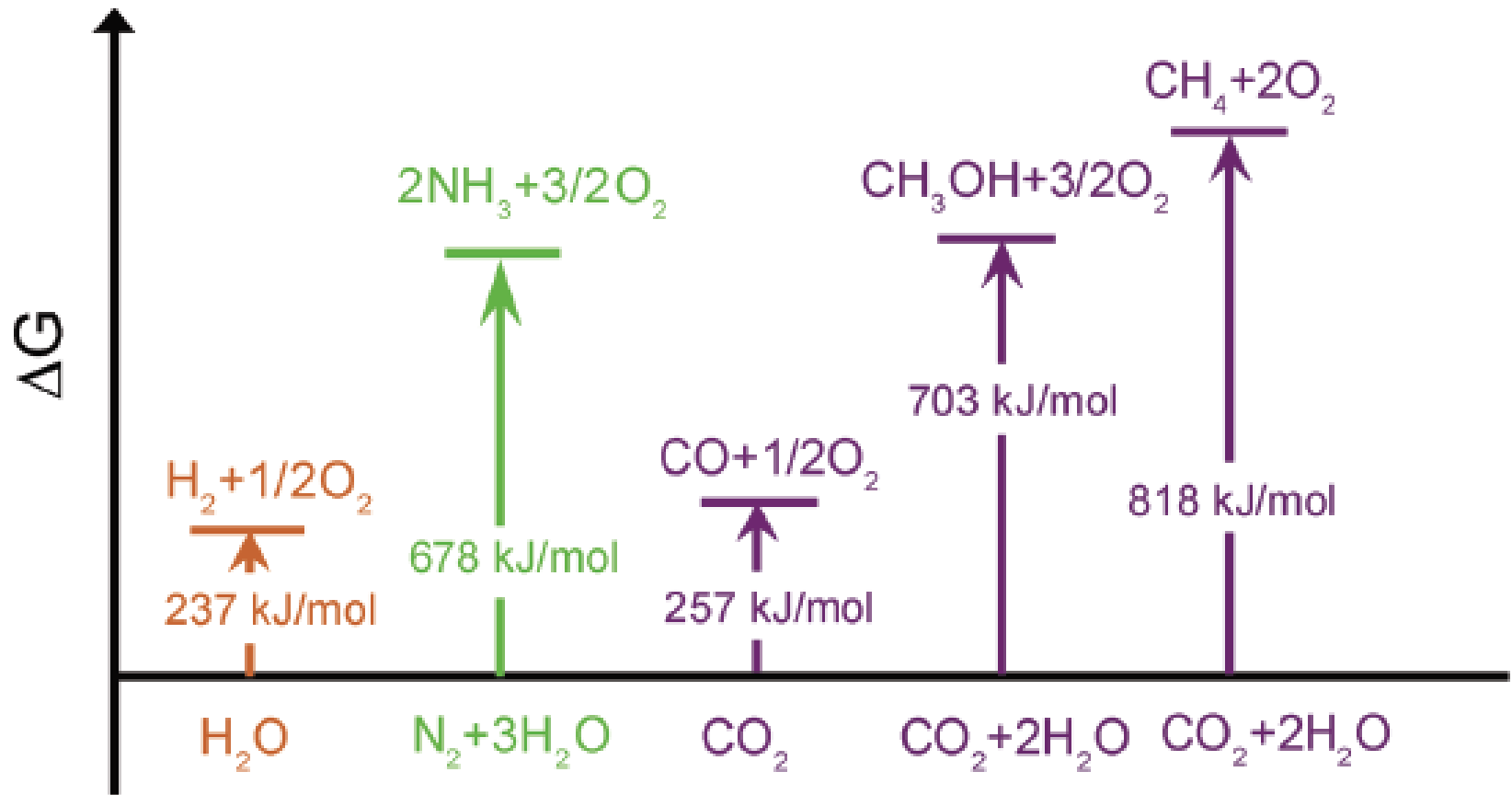


Significato più **ampio**

«.. 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

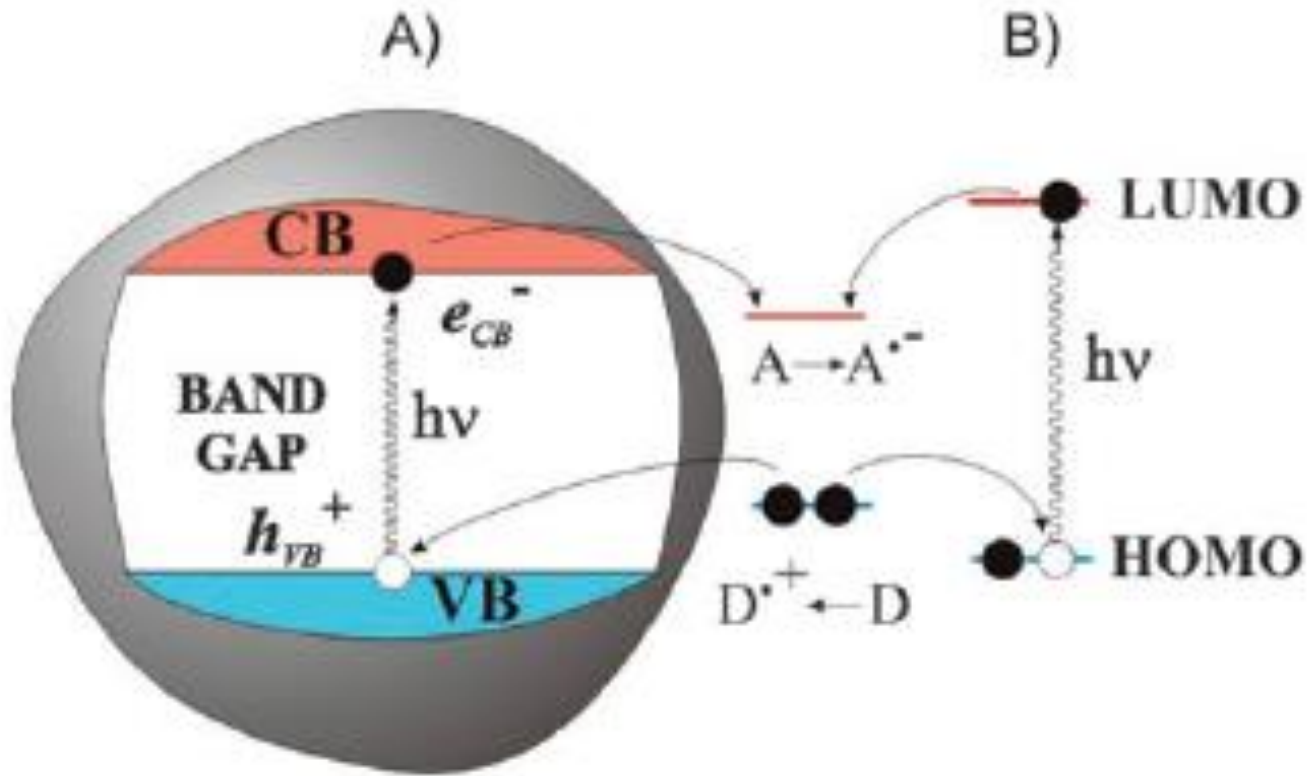




# Stadi nei processi fotocatalitici

Fotocatalisi eterogenea

Fotocatalisi omogenea

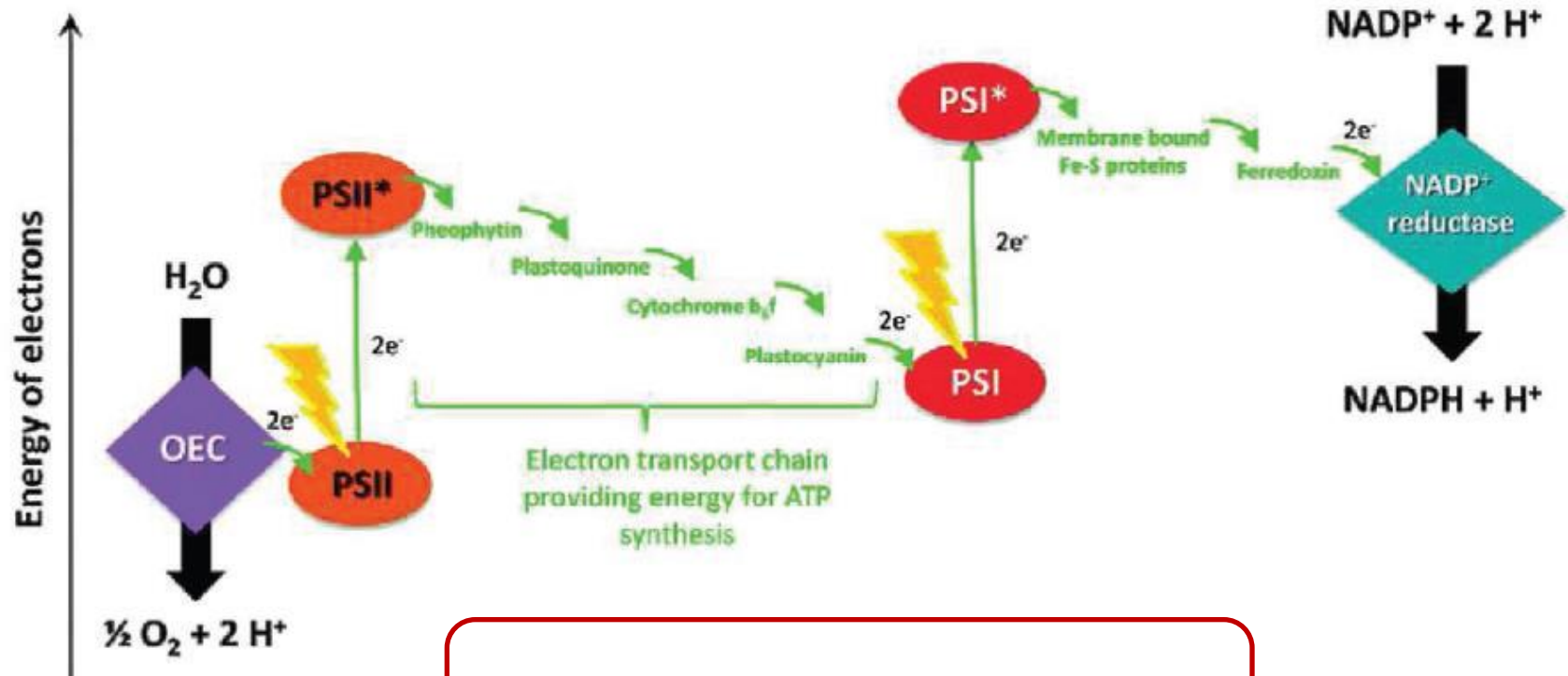


TON

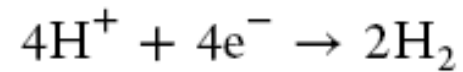
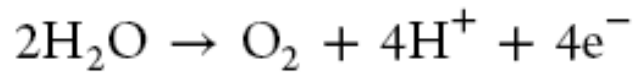
TOF

$\Phi$

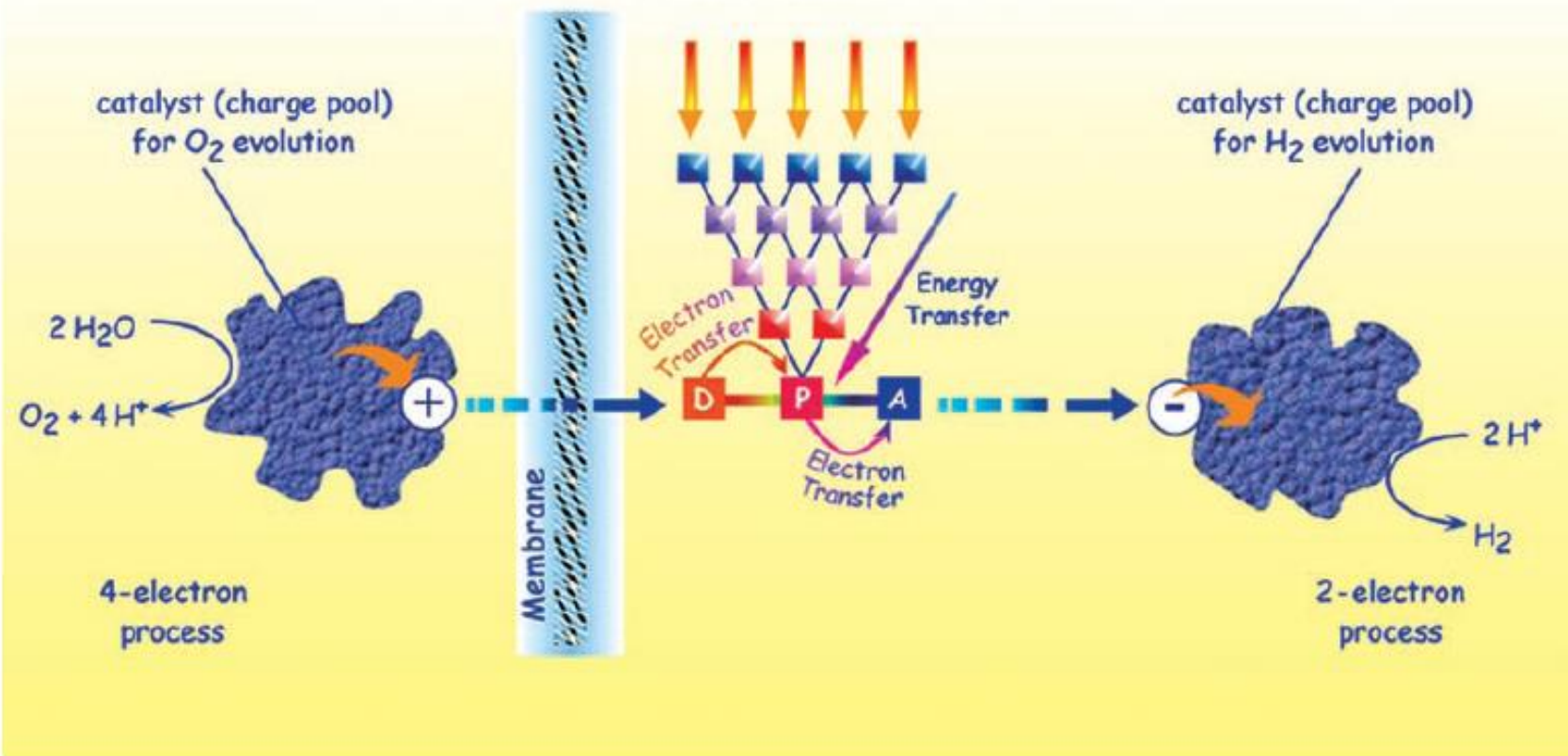
# Fotosintesi naturale



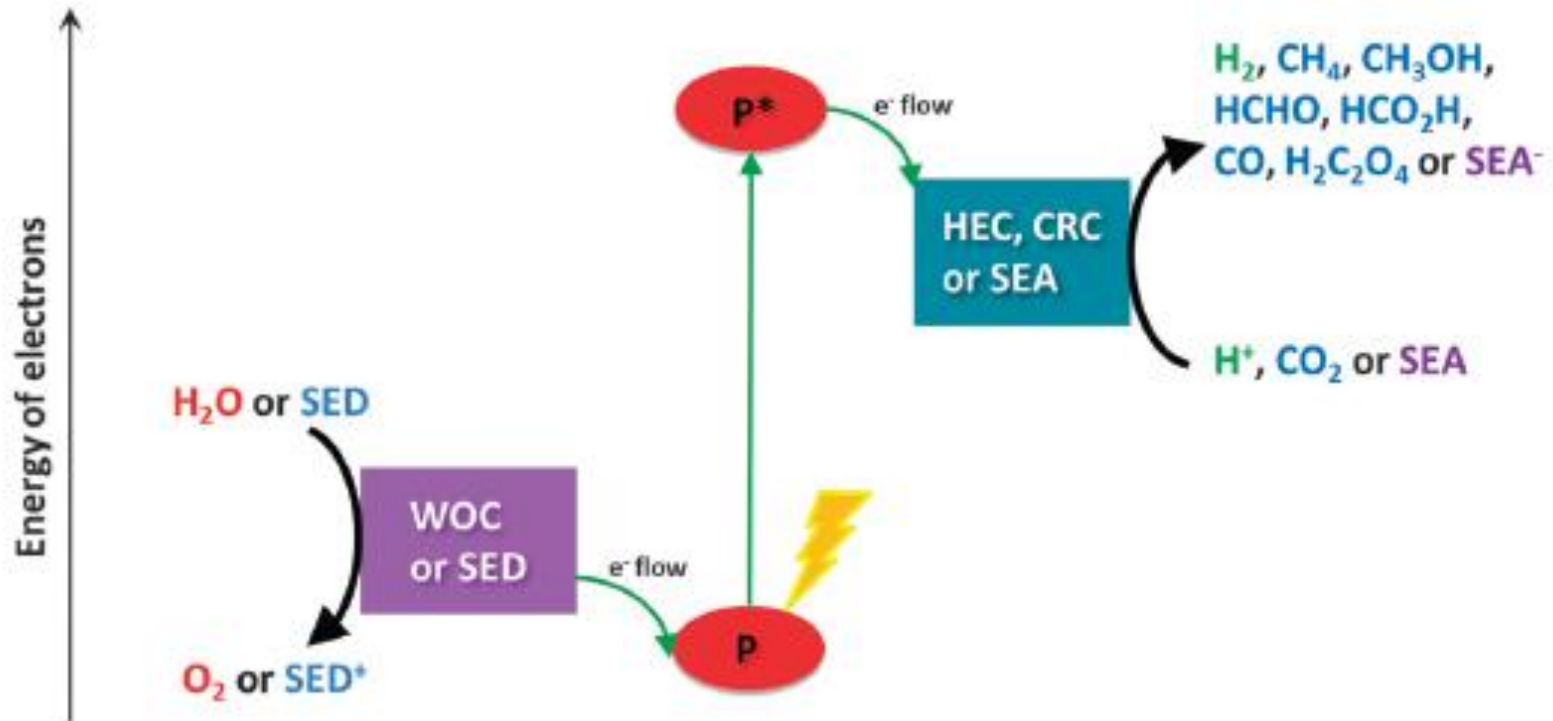
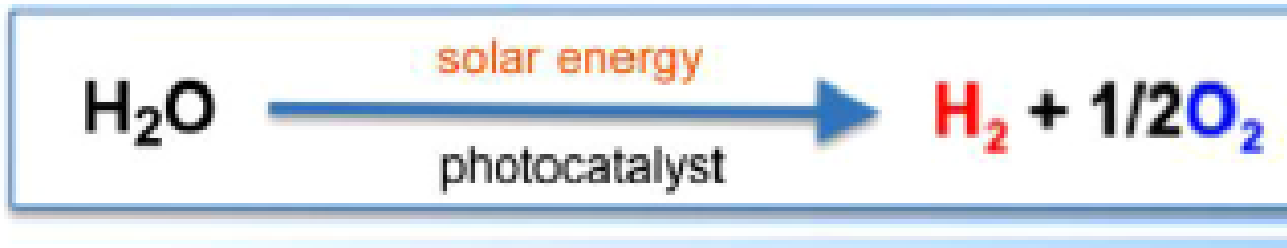
# Fotosintesi artificiale



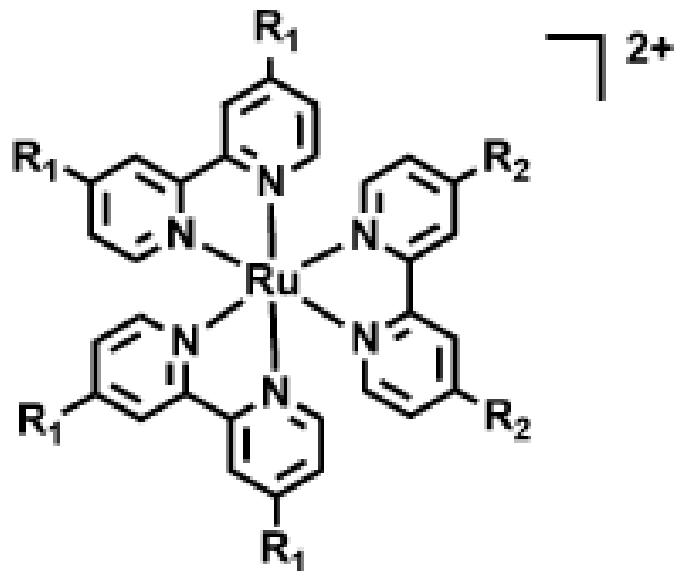
Light Absorption



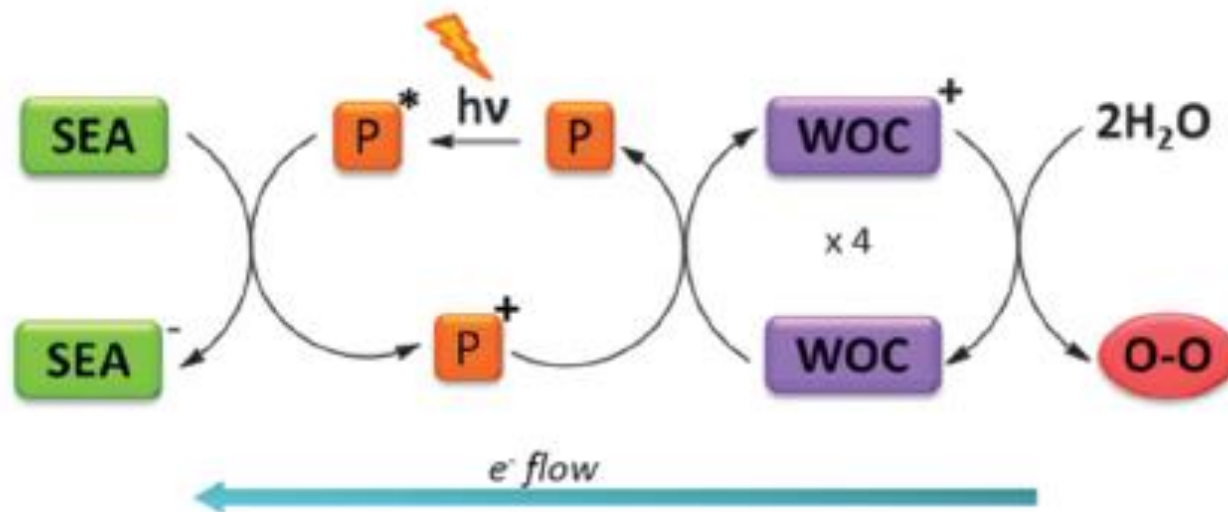
# Fotosintesi artificiale



# *I fotosensibilizzatori*



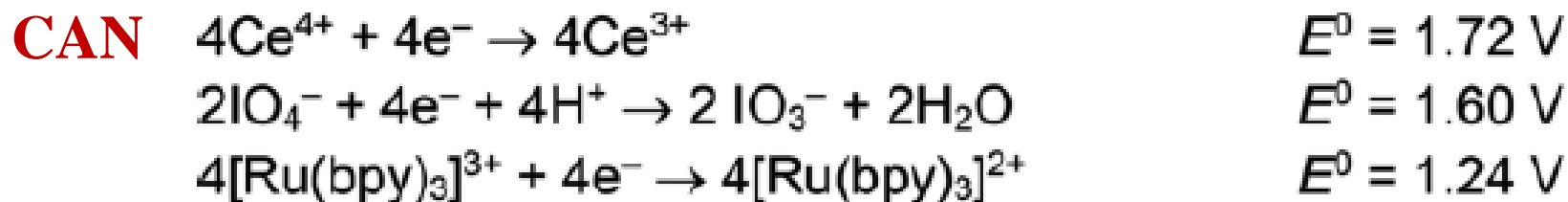
- Absorption at 452 nm (visible light)
  - Stable, long-lived excited state ( $\tau = 1100$  ns)
  - Single electron transfer (SET) catalyst
  - Effective excited state oxidant and reductant
- Miglior ossidante e miglior riducente per 2.12 V**



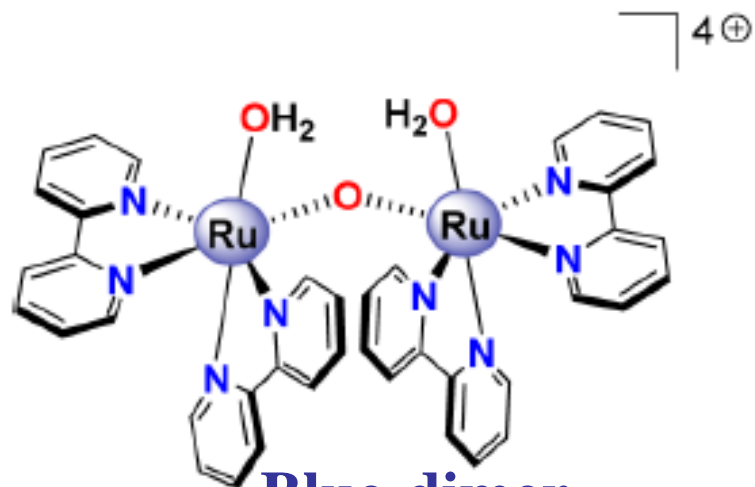
# *Water oxidation catalysis*



## **SEA** più utilizzati

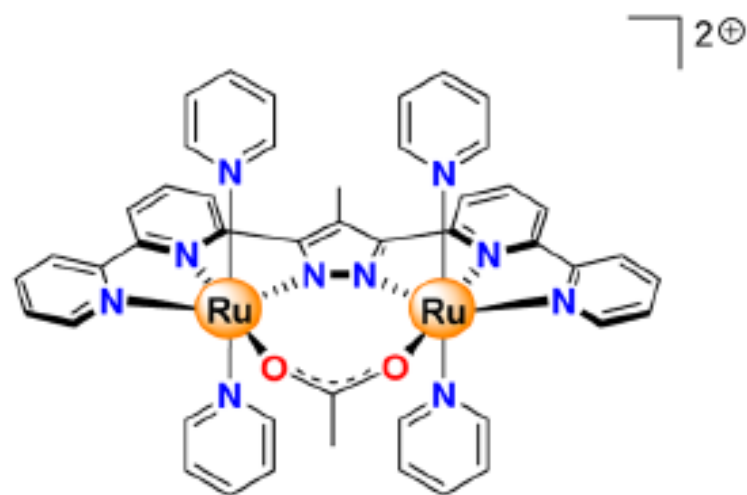
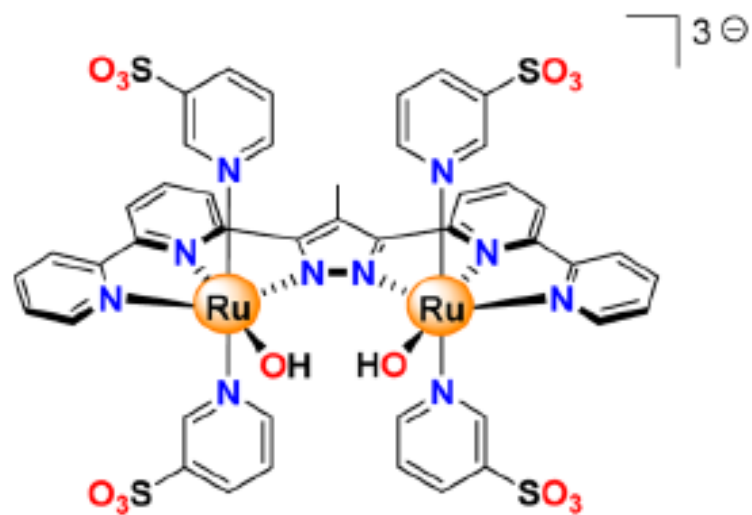
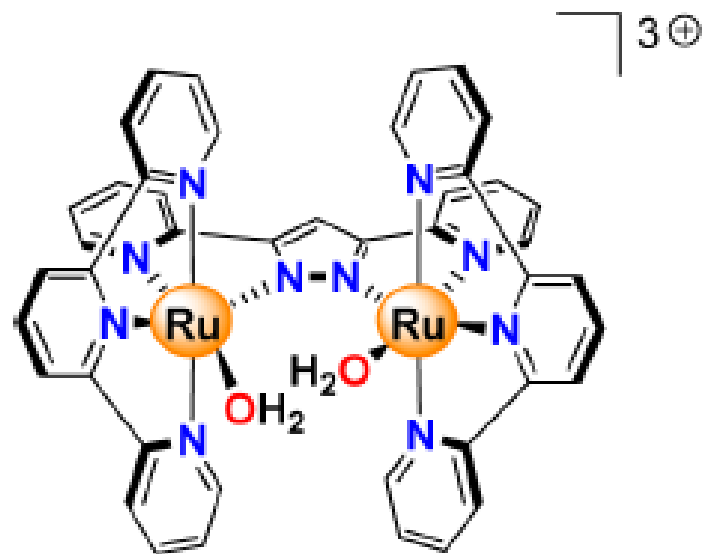


# Ru-based Water Oxidation Catalysts



Blue-dimer

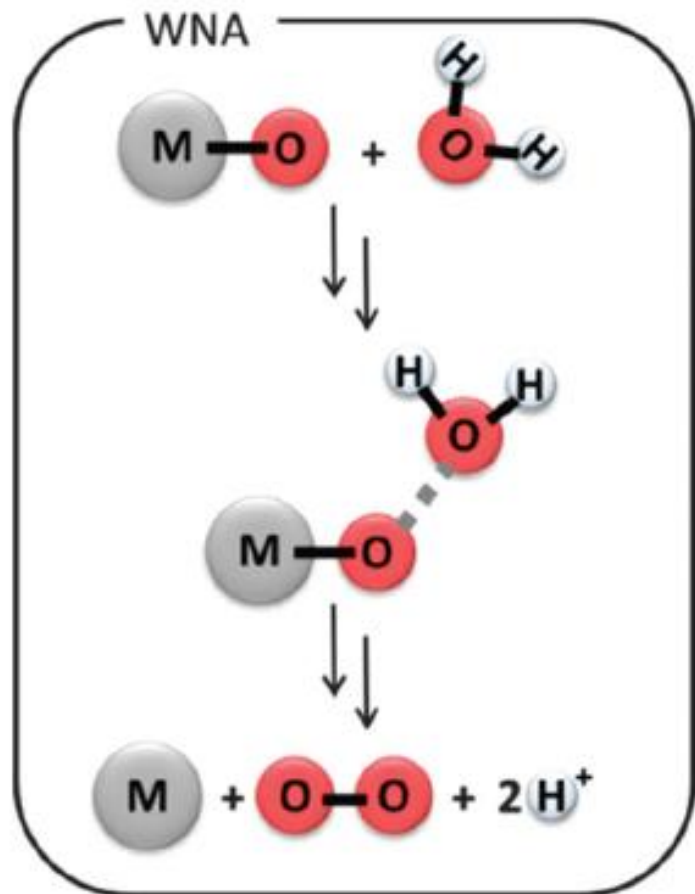
$$\text{TON} = 13.2 \frac{n_{\text{O}_2}}{n_{\text{cat}}}$$



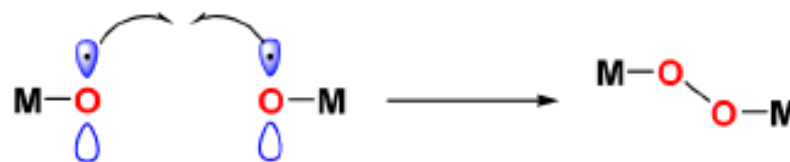
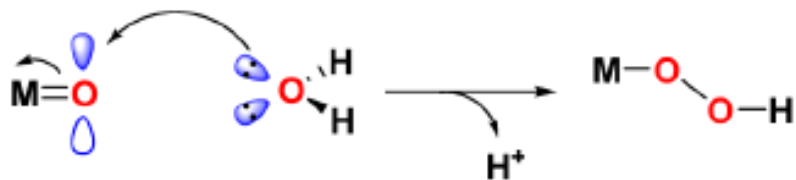
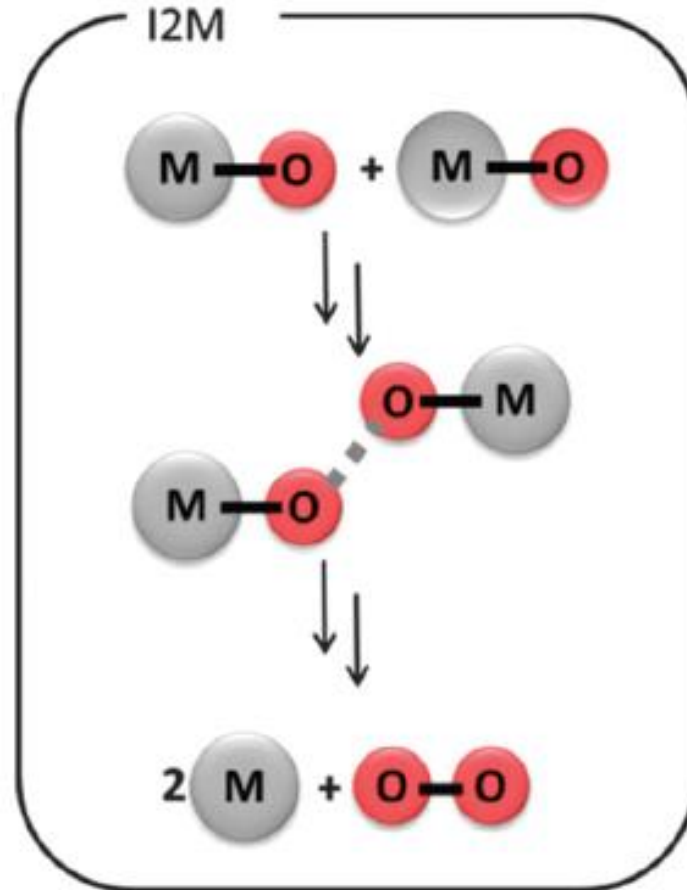
# Possible mechanisms

Water nucleophilic attack

Interaction between two M-O units

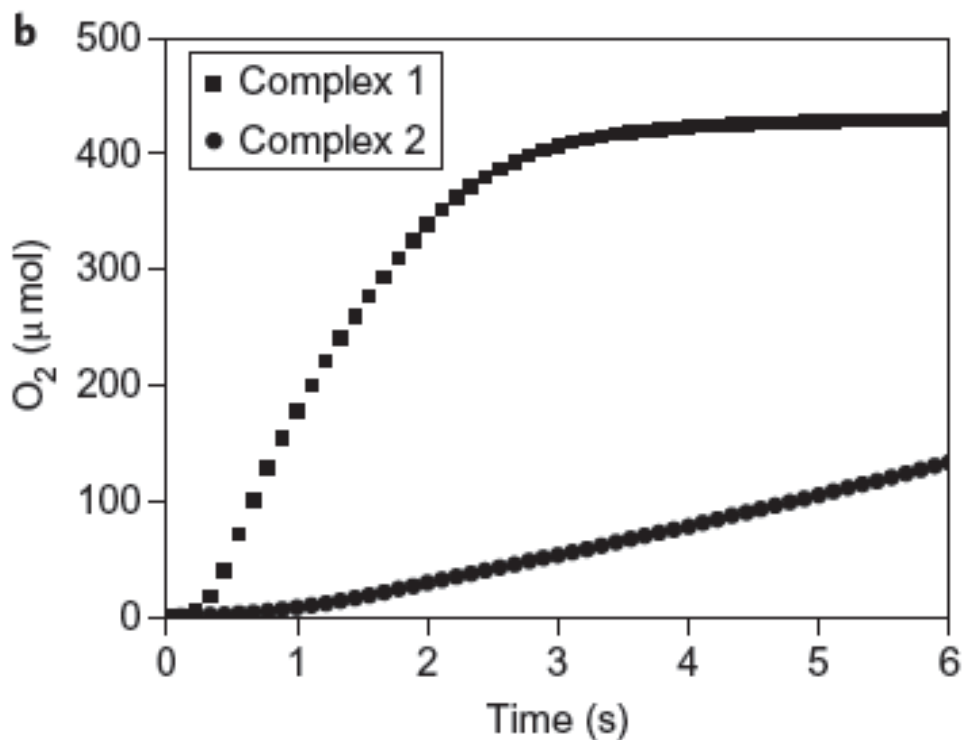
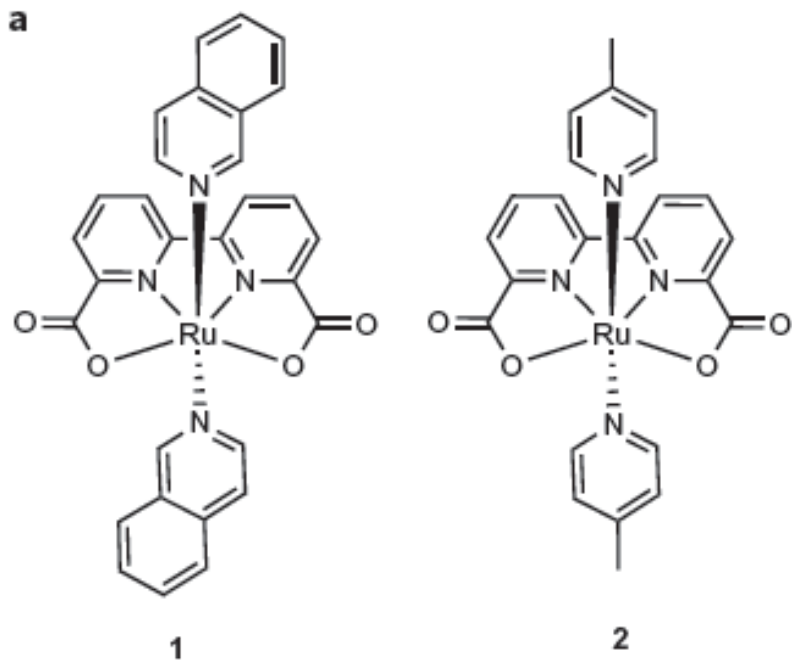
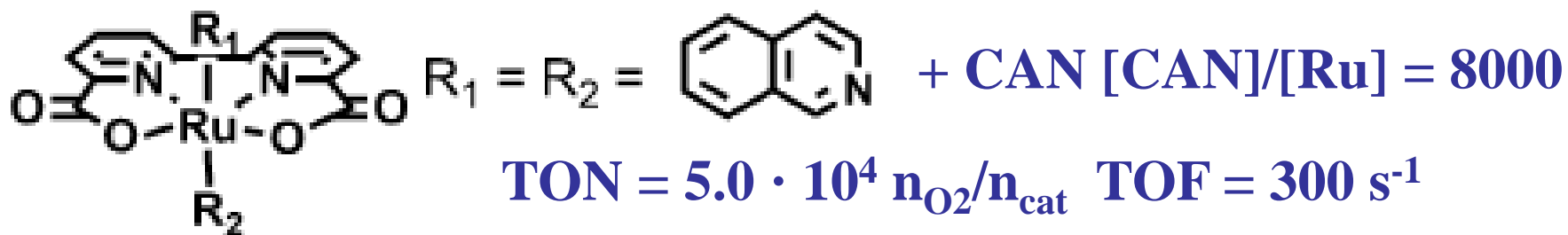


or



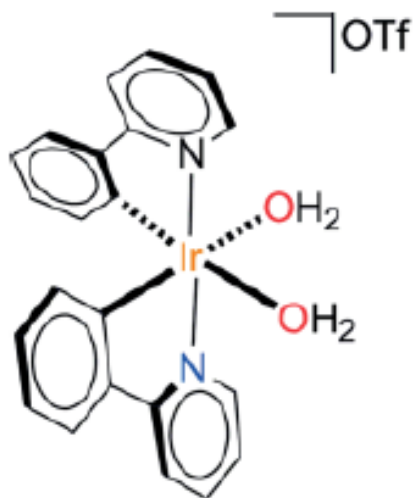


# Ru-based Water Oxidation Catalysts

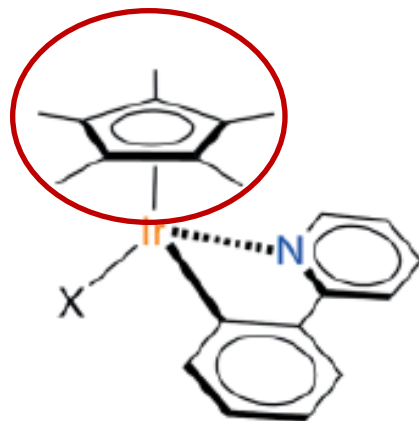




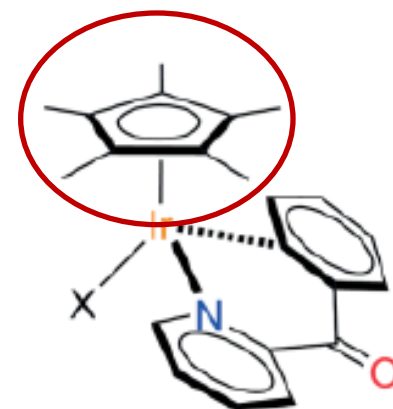
# *Ir-based Water Oxidation Catalysts*



1, Bernhard 2008

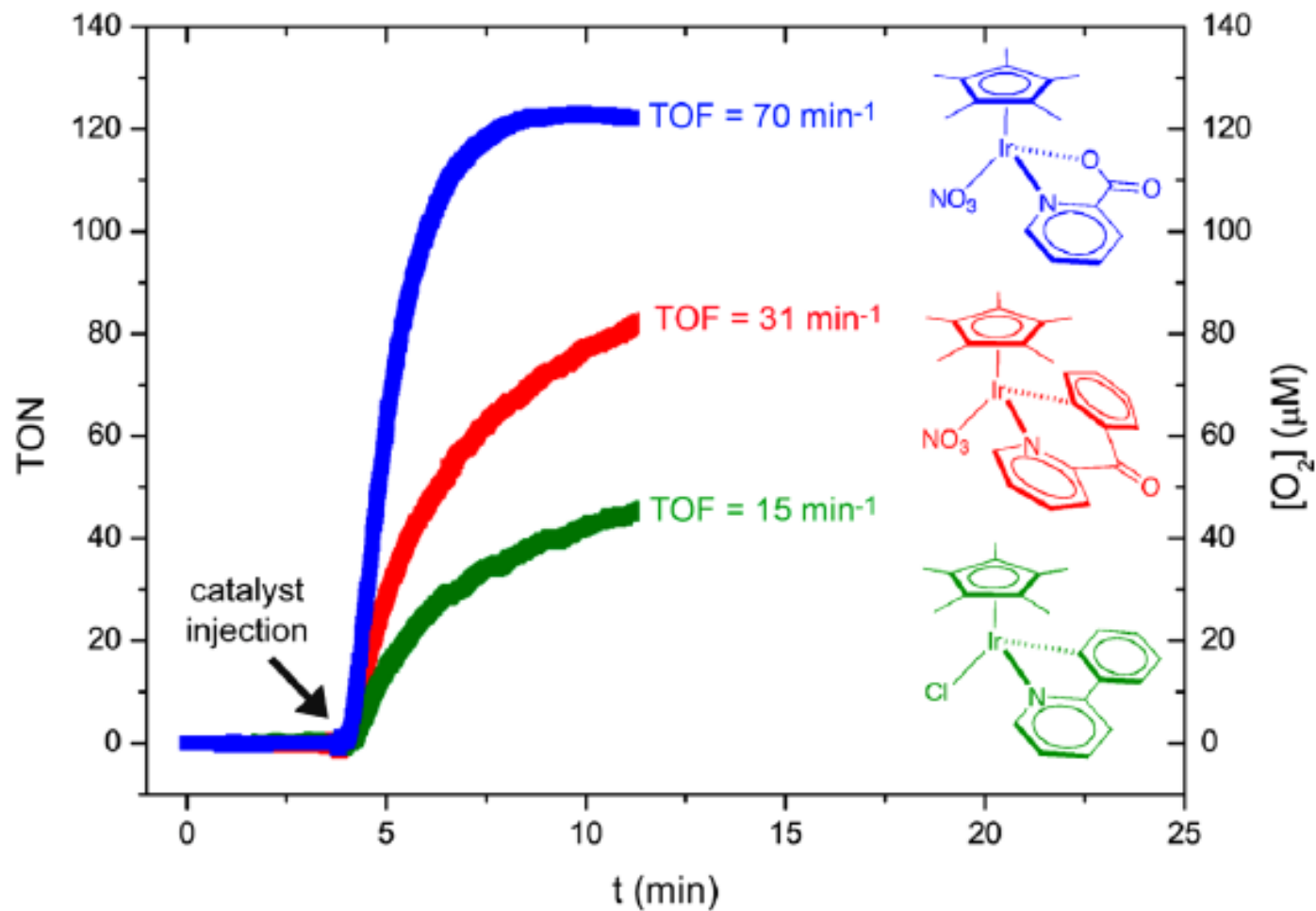


2, Crabtree 2009



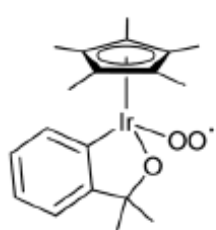
3, Macchioni 2010

# *Ir-based Water Oxidation Catalysts*

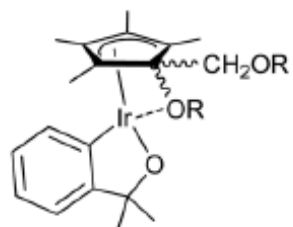


**Condizioni di reazione:**  $[\text{CAN}]/[\text{Ir}] = 40\ 000$ ;  $\text{pH} = 1$  per  $\text{HNO}_3$ ;  $T = 25\ ^\circ\text{C}$ ;  $\text{H}_2\text{O}$ .

# Possible mechanisms

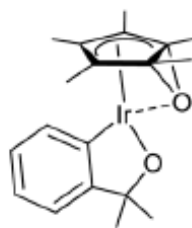


24

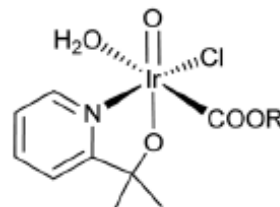


25

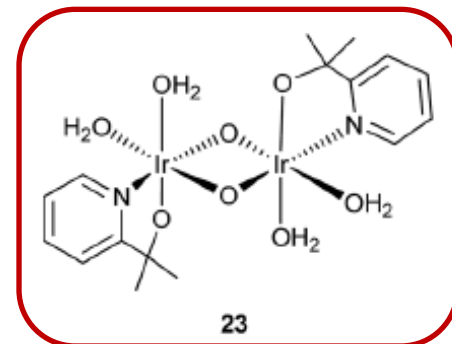
R = H or OH



26



27

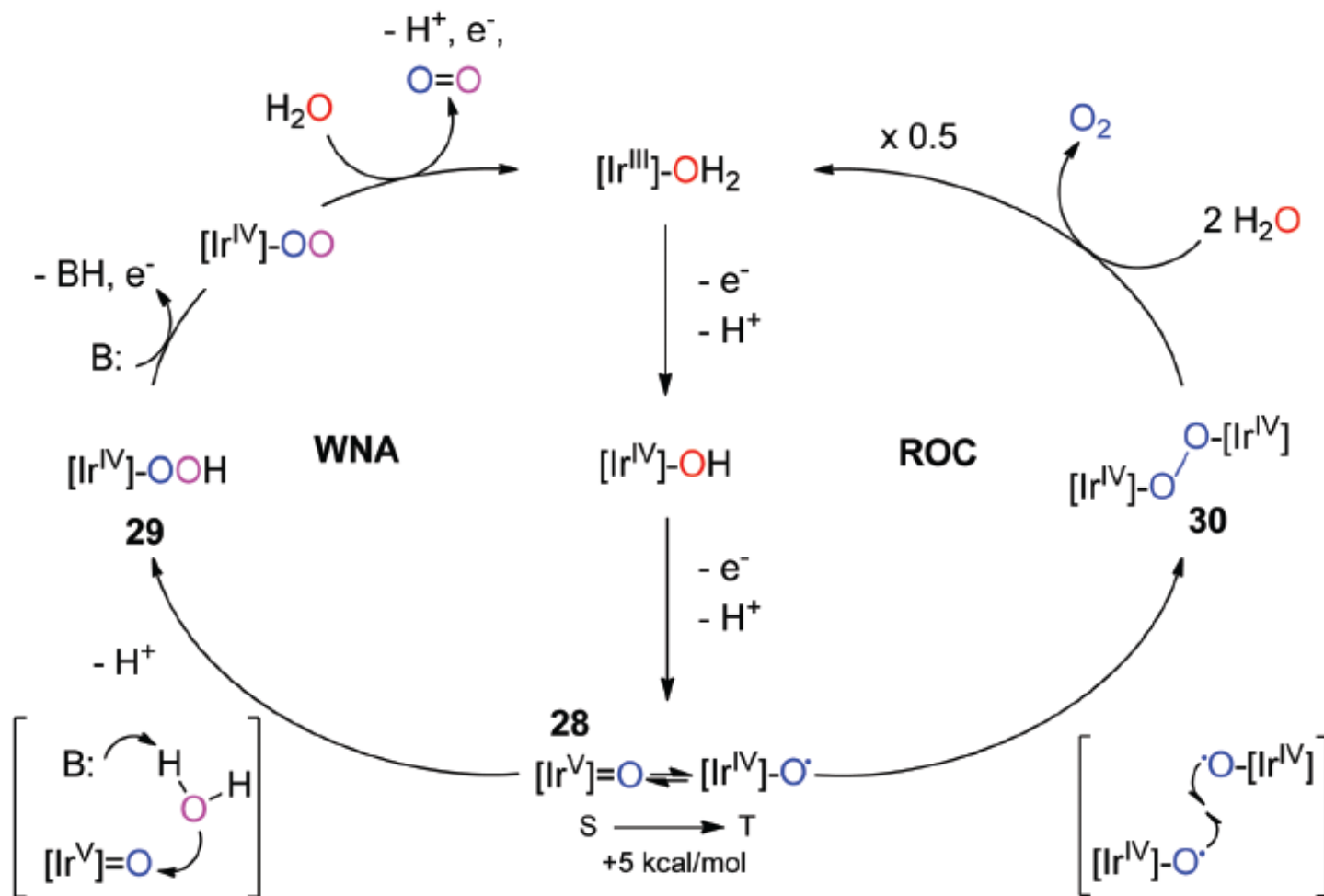


23

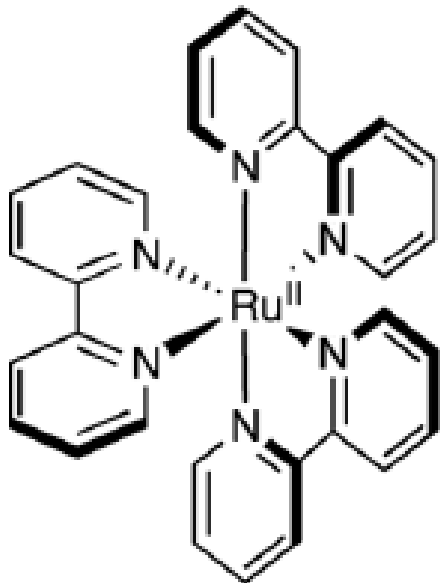
*Cp\* intact*

*fully oxidized*

# Possible mechanisms



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

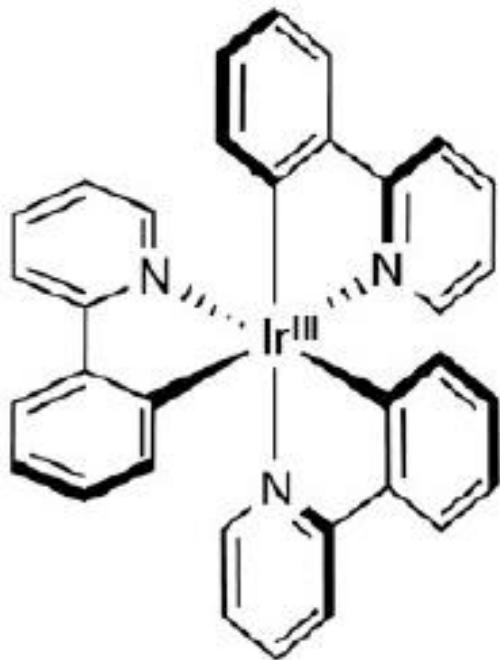


- Absorption at 452 nm (visible light)
- Stable, long-lived excited state ( $\tau = 1100$  ns)
- Single electron transfer (SET) catalyst
- Effective excited state oxidant and reductant

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

> **30 applicazioni in sintesi organica** tra reazioni di riduzione, ossidazione, redox, e reazioni di energy transfer

# *[Ir(N-C)<sub>3</sub>]: un catalizzatore fotoredox molto versatile*



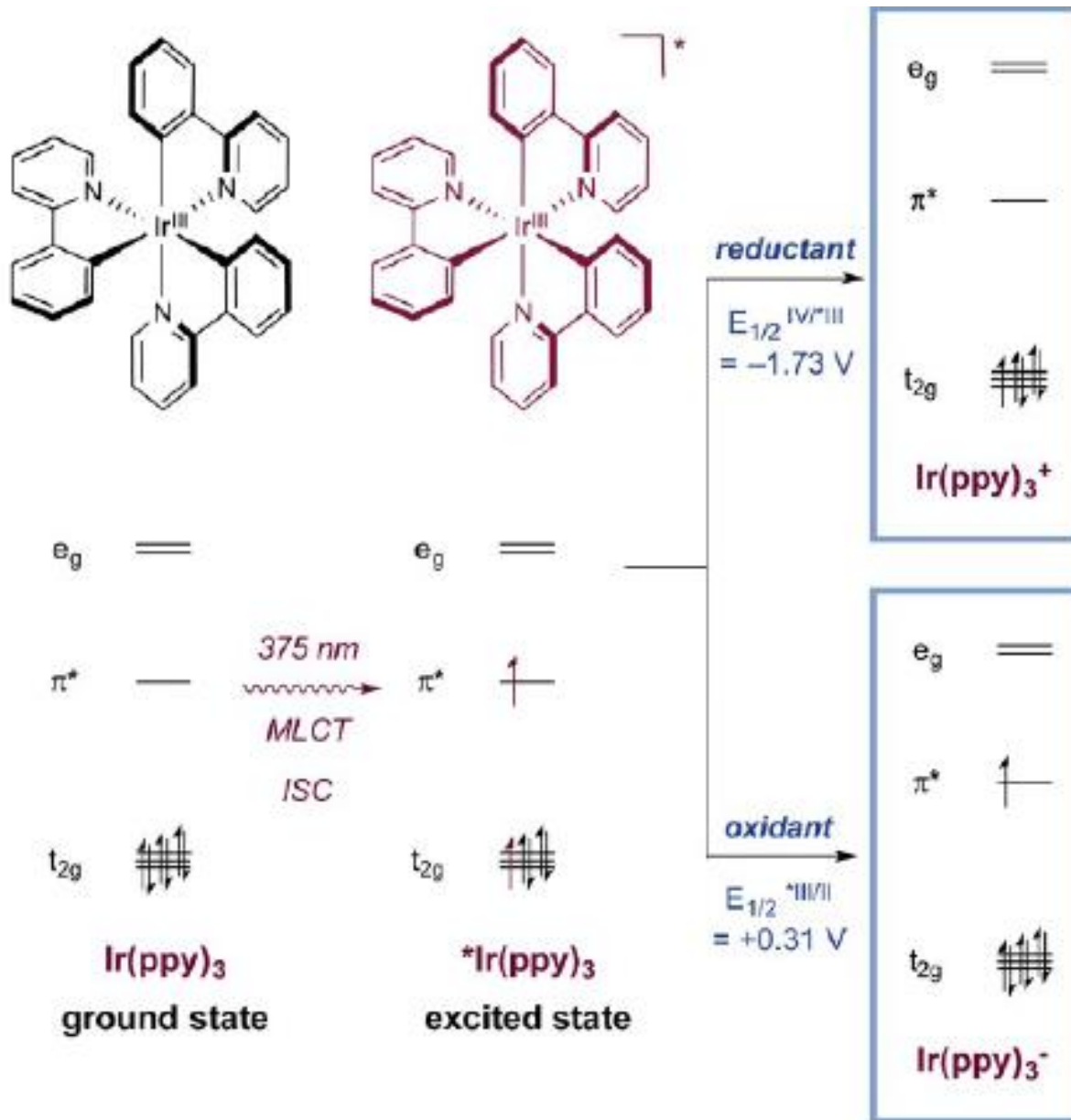
**Ir(ppy)<sub>3</sub>**

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

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

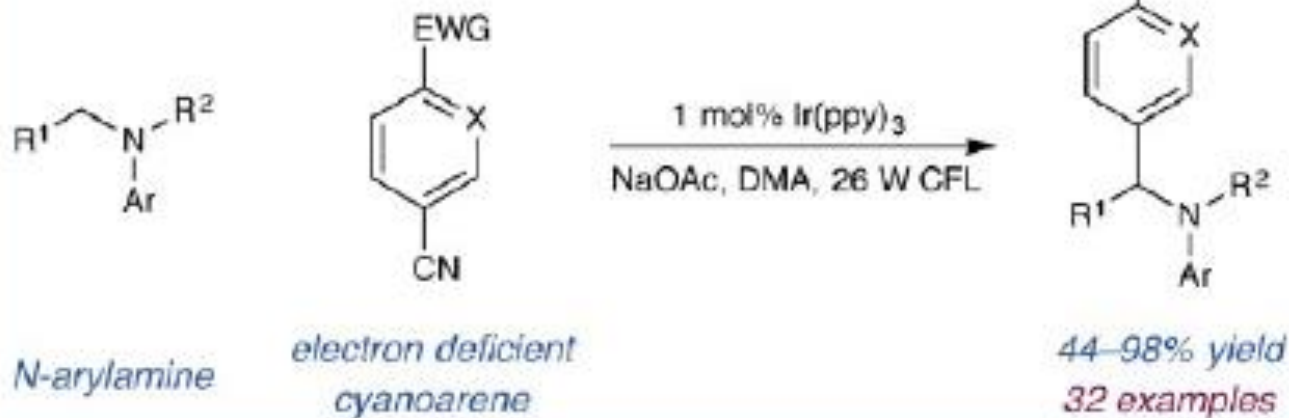


# $[\text{Ir}(\text{N-C})_3]$ : schema semplificato degli MO



# Sintesi di amine con areni in alfa

## Amine $\alpha$ -arylations via radical-radical coupling



# Sintesi di amine con areni in alfa

