

LIGHT MATTER INTERACTIONS - DEVELOPMENT OF SMART PHOTOACTIVE MATERIALS FOR ENVIRONMENTAL APPLICATIONS

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Light-matter interactions

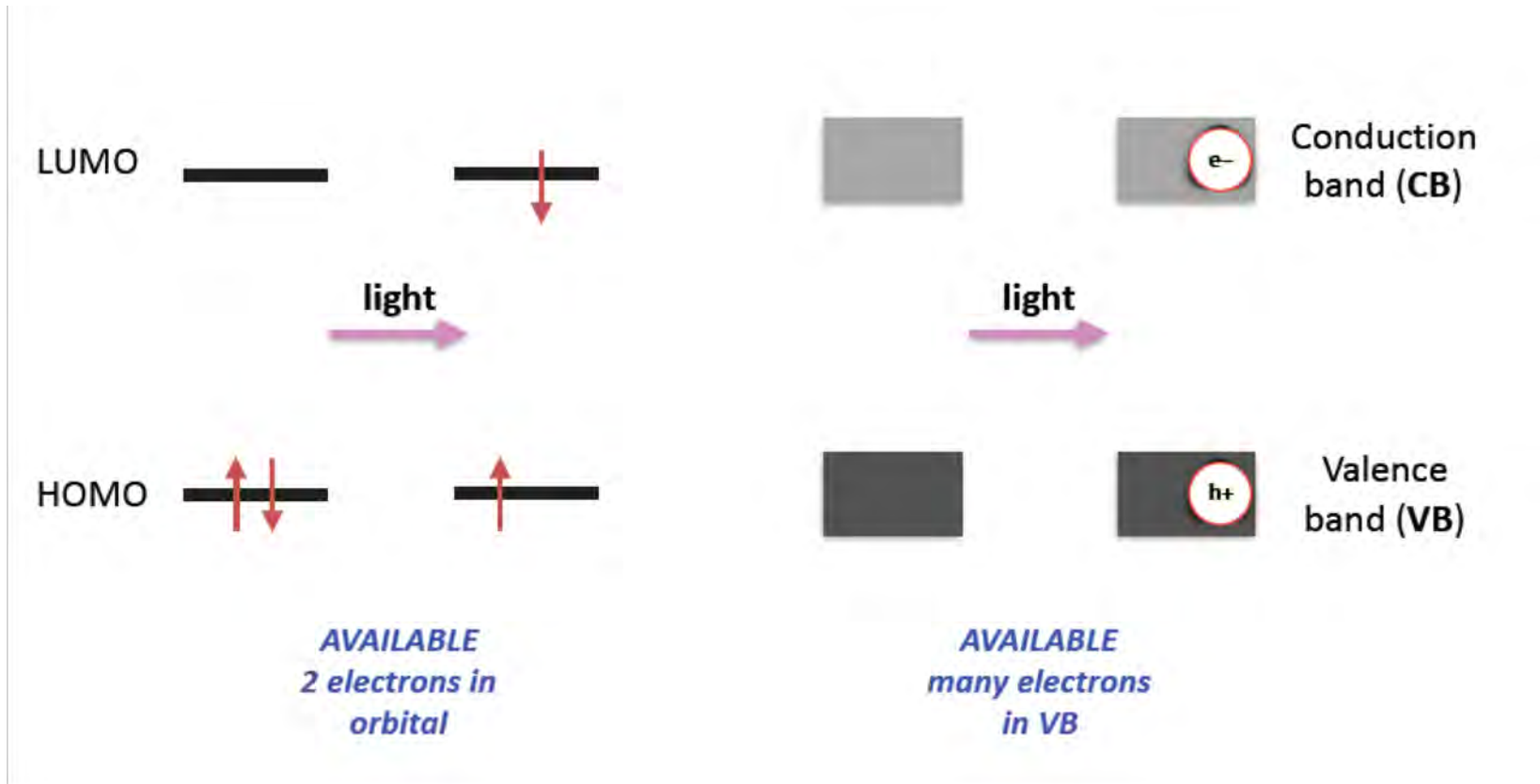
**Development of smart photoactive materials
for environmental applications**



Semiconductors and fluorescent nanomaterials

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Band theory of solids: molecules vs semiconductors



Semiconductor properties and applications



- Electroluminescence from semiconductors
- Conductivity
- Doping: n-doped and p-doped semiconductors. Diodes.
- TiO_2 : from synthesis to applications.
 - Water purification
 - Sunscreens
 - Catalysis
- Other semiconductors: quantum dots
 - Synthesis
 - Optical properties
 - Bio-labeling
 - QLED: QD displays

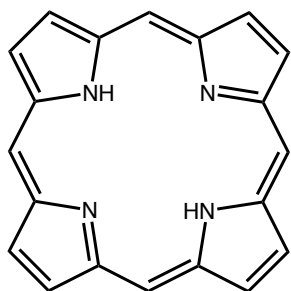


Design of Phthalocyanine for use as photosensitizers (photocatalysts)

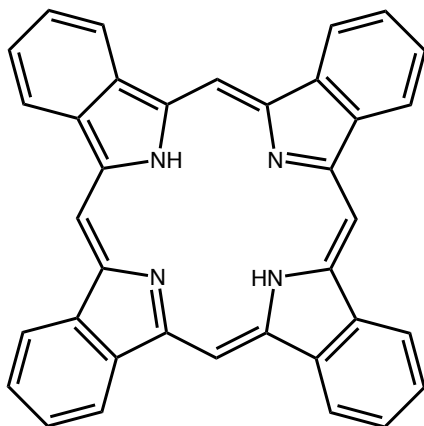
Prof. Tebello Nyokong



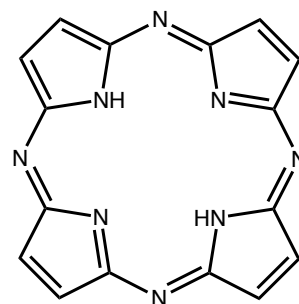
Introduction to Porphyrin-type molecules



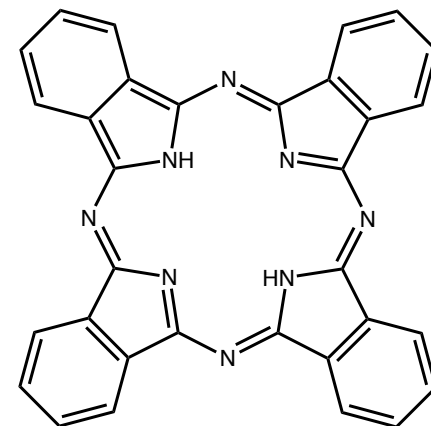
Porphyrin



**Tetrabenz
Porphyrin**



**Tetraaza
porphyrin**



**Phthalocyanine:
Tetrabenz-tetraaza
porphyrin**



Introduction to Phthalocyanines (PCs)

- Molecular properties
- Traditional & new applications
- Photophysical properties of PCs:
Phosphorescence Quantum yield and Single oxygen quantum yields. Laser Flash Photolysis
- Photosensitization involving metal-PC complexes:
 - Phototransformation of pollutants
 - Phototransformation of alkenes: fine chemicals
 - Photodynamic therapy (PDT)
 - Photodynamic Antimicrobial Chemotherapy (PACT)
 - Drug delivery



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Introduction to Photochemistry

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Photochemistry can be described as the chemistry of the excited state



It is usually accompanied (that is, competitive) with processes that return the excited state to the ground state and are described as **photophysics**

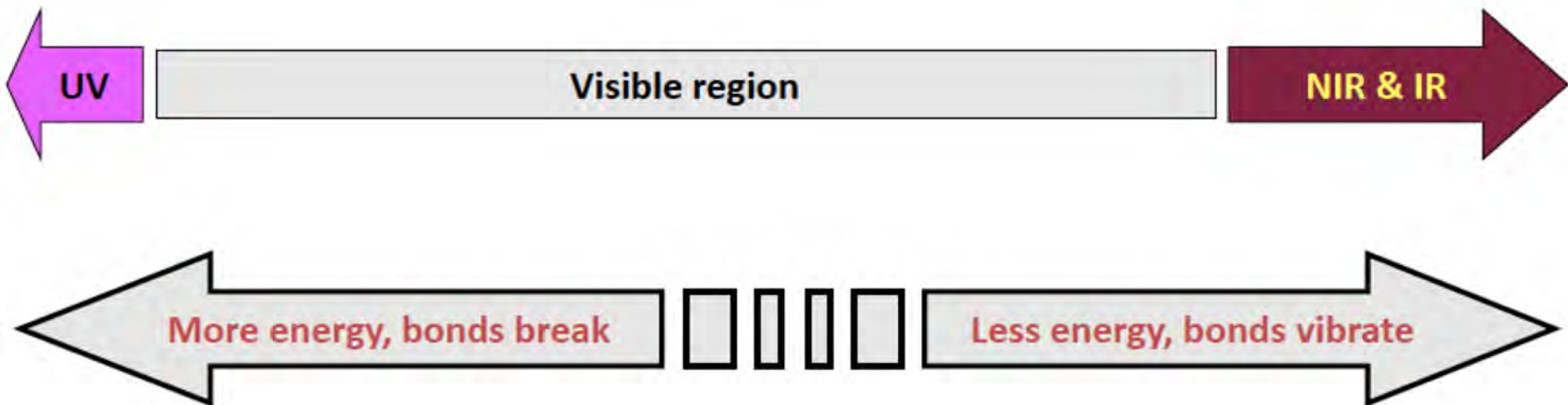
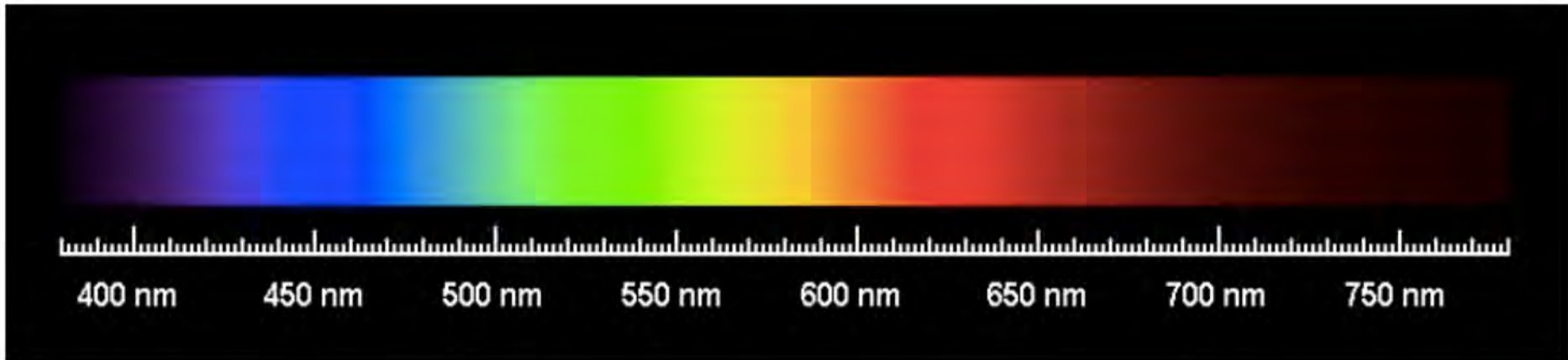
In the first few slides we will assume that electron spin is conserved in all cases. We will later learn that some of the most interesting photochemistry involves precisely electron spin changes

The two most common **photophysical** processes are:

- Radiationless transitions, in which the interconversion to the ground state simply converts light into heat
- Luminescence in which the energy is returned at least in part as light

Our first goal will be to understand the absorption of light, its consequences, and the importance of the wavelength (color) of the light.

Wavelength & color



Photochemistry



- Solar spectrum and eye sensitivity
- The spectrum in biology language
- Photochemistry
 - The first law of photochemistry
 - Jablonski diagram
 - Formaldehyde MO ordering
 - Kasha's rule
 - Fluorescence quantum yield
 - Frank-Condon principle
 - Fluorescence spectrum and lifetime
 - Stokes shifts
 - Energy transfer:
 - Trivial energy transfer
 - Electron exchange processes
 - Förster energy transfer (FRET)



Three classic molecules

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Excited state complexes



Two identical molecules:

EXCited diMER \longrightarrow EXCIMER

Two different molecules:

EXCited comPLEX \longrightarrow EXCIPLEX

Ground state complex



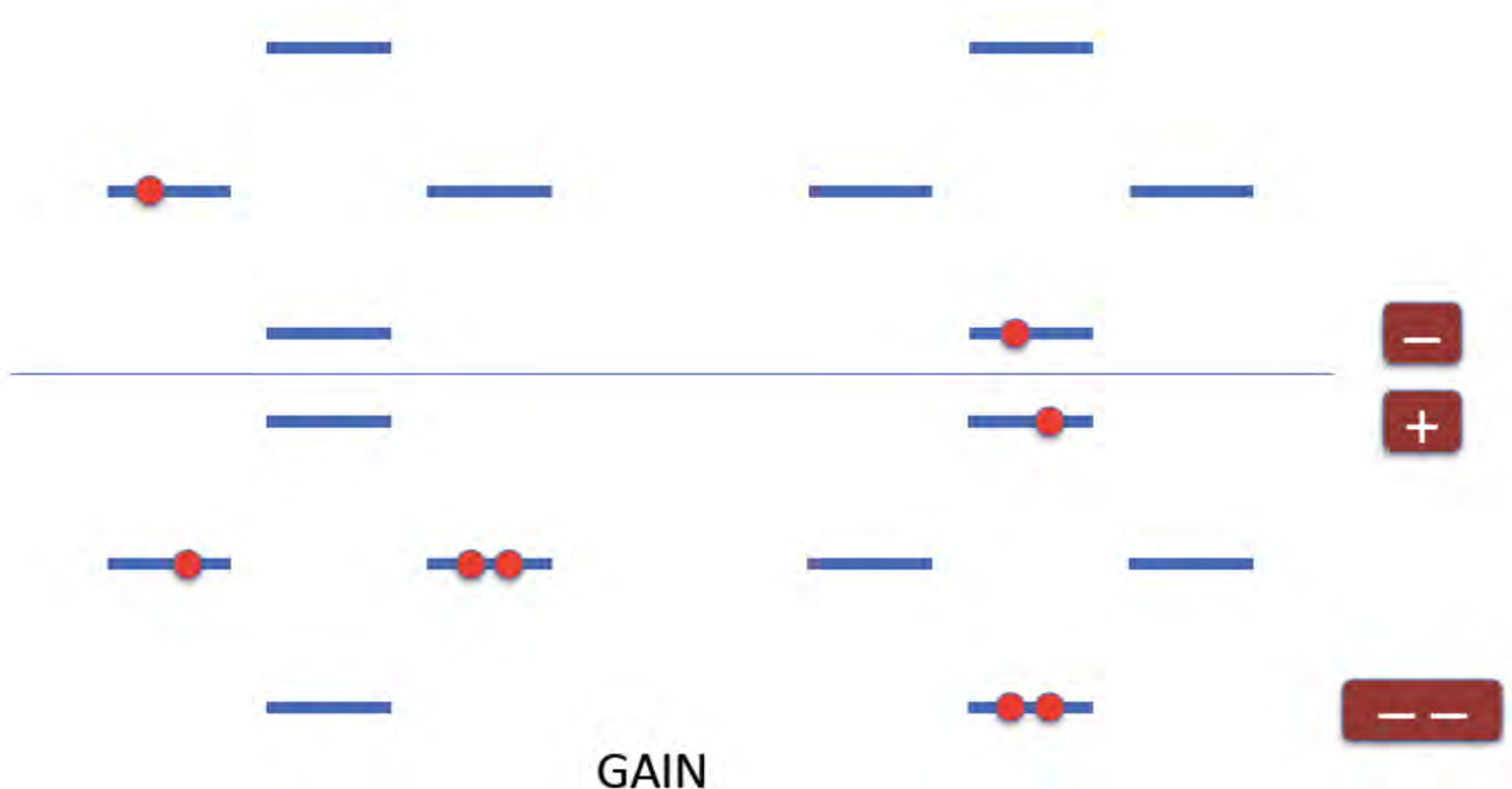
Association always leads to a negative entropy change ... that is, entropy does not help with the free energy change for association:

$$\Delta G = \Delta H - T\Delta S$$



NO GAIN

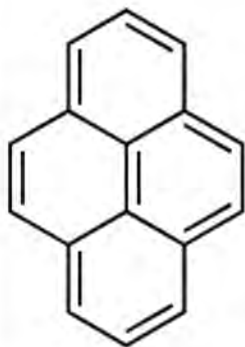
Excited state complex



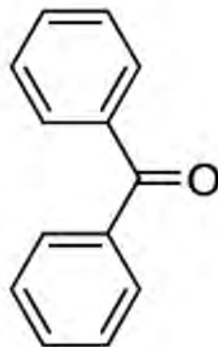
Interacting orbitals



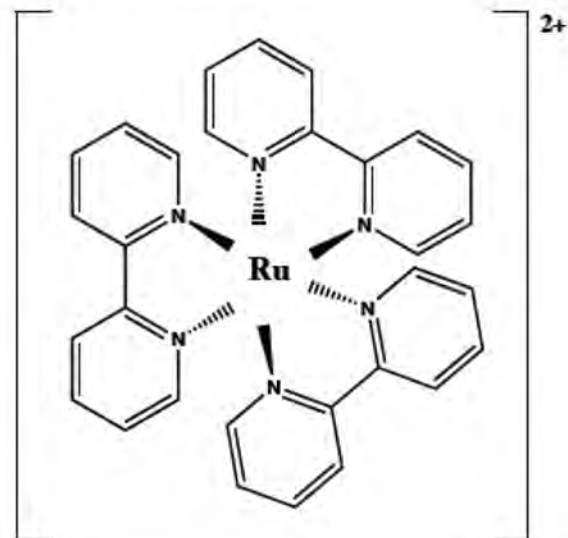
Three classic



Pyrene fluoresces with great efficiency, forms excimers and is a great polarity sensor



Benzophenone does most of its chemistry from the triplet state, frequently behaving as a free radical



$[\text{Ru}(\text{bipy})_3]^{2+}$ has nice visible absorption, long emission lifetime and is a good candidate for redox chemistry



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Photoredox catalysis

with more concepts on electron transfer

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Redox properties of excited states

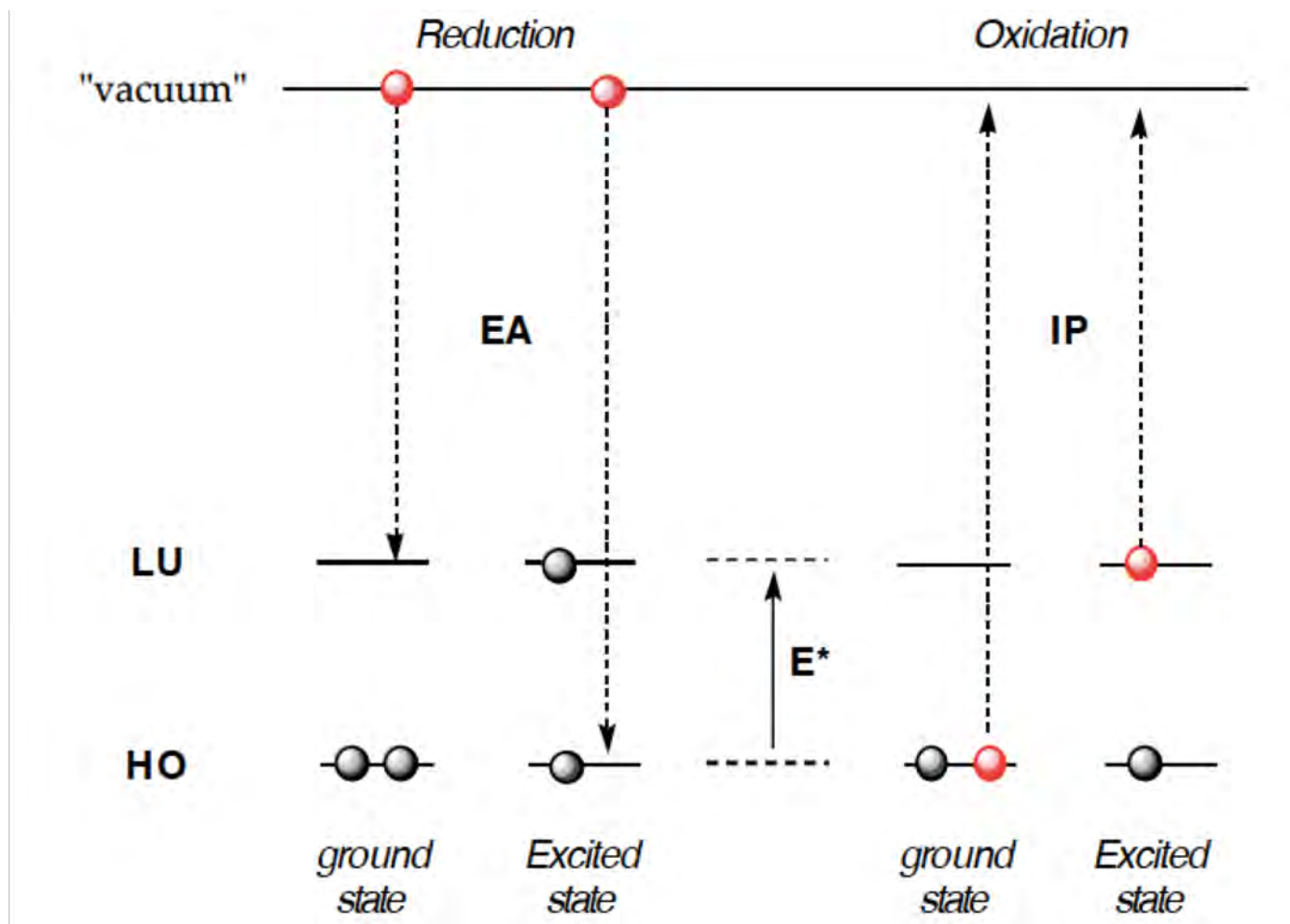


Excited states of diamagnetic molecules with closed shell ground states are always better oxidizing and reducing agents than their corresponding ground states

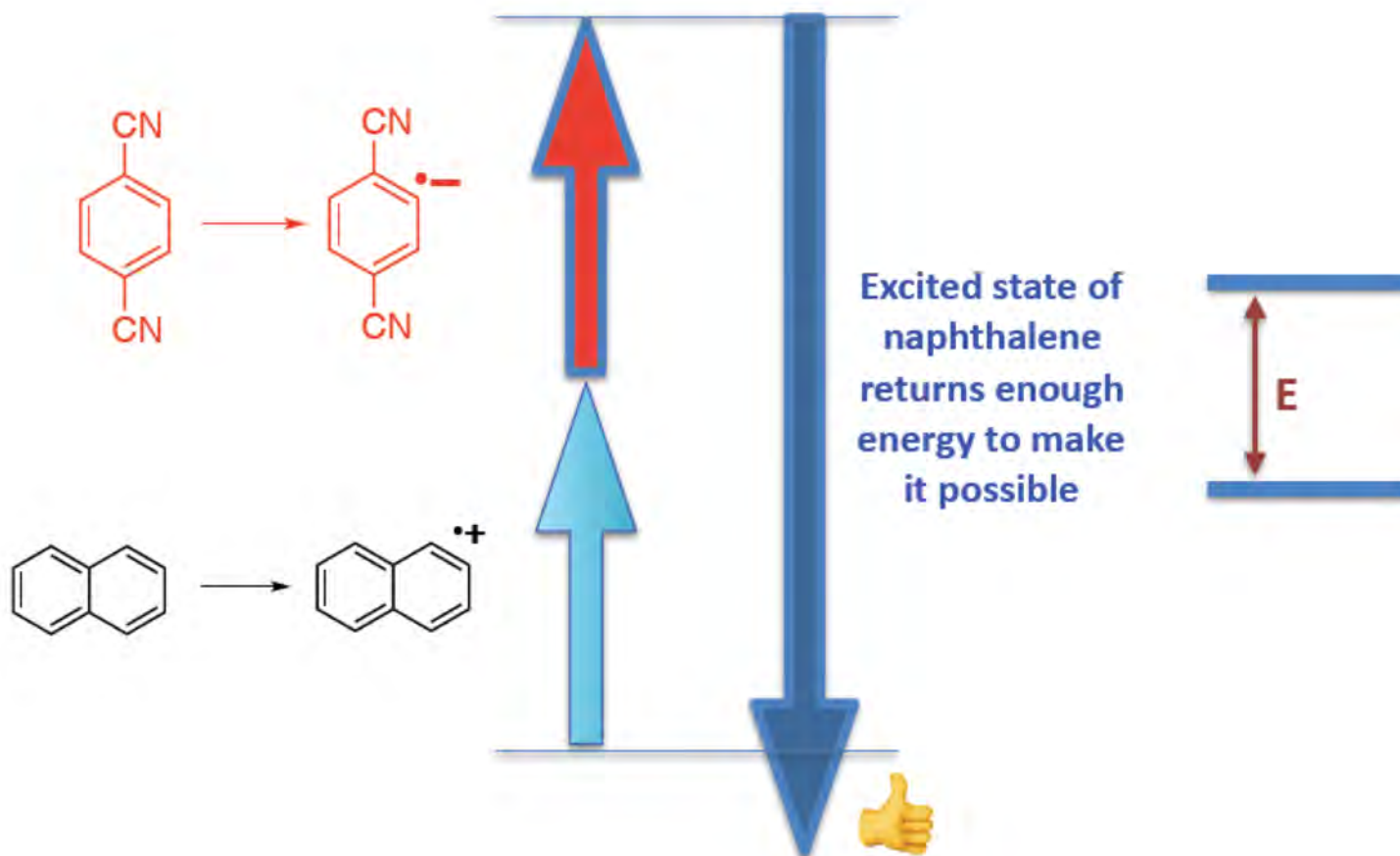
This is not necessarily true of species with open shell ground states such as radicals and O₂

Sometimes we may need to worry that a molecule that is not prone to electron transfer in the ground state does so readily in the excited state. This is another form of quenching

Redox properties of excited states



Excited state electron transfer *the excited state pays the energy bill*



Photoredox catalysis



Using the concepts of electron transfer theories

Three key aspects of catalyst action



(For any type of catalysis)

1. Taking part in the reaction

- it will change itself during the process by interacting with other reactant/product molecules

2. Altering the rates of reactions

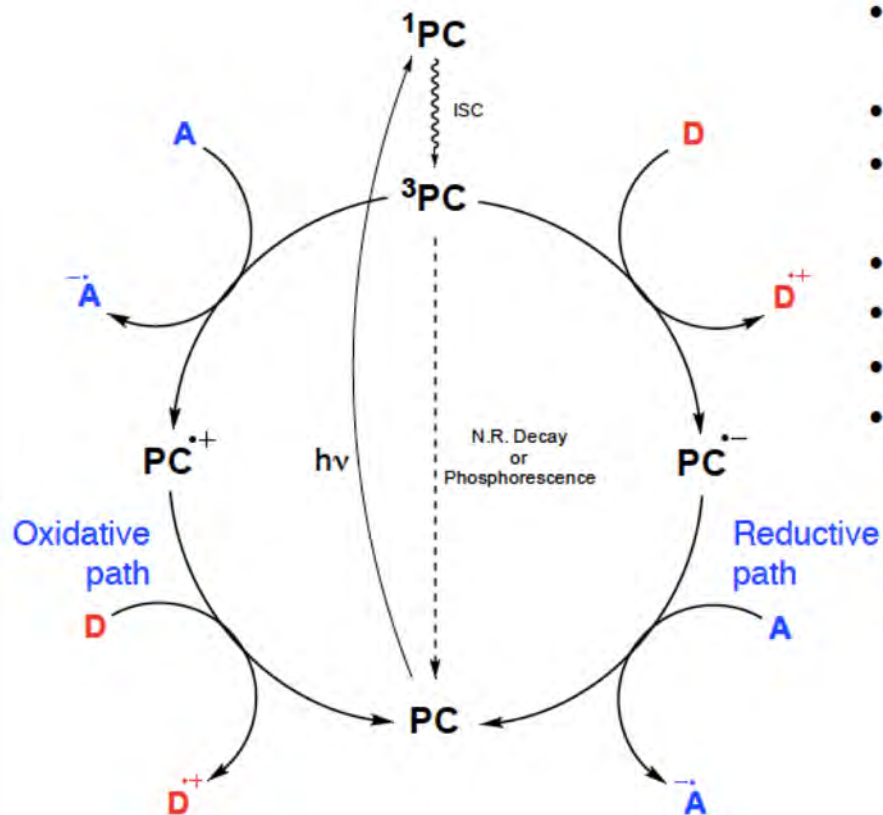
- in most cases the rates of reactions are increased by the action of catalysts; however, in some situations the rates of undesired reactions are selectively suppressed

3. Returning to its original form

- After reaction cycles a catalyst with exactly the same nature is 'reborn'
- In practice a catalyst has its lifespan - it deactivates gradually during use



Photoredox catalysis



Improving Photoredox Catalysis

- Start with expensive transition metal catalysts
- Move to cheaper organic dyes
- develop inexpensive heterogeneous catalysts
- Achieve easy separation/recovery
- Enable catalyst recycle/reuse
- Adapt to flow chemistry
- Scale up

A look at the “engine” that runs photocatalysis, frequently $Ru(bpy)_3^{+2}$ and $EtNiPr_2$

Photoredox catalysis



- Redox properties of excited states
- Rehm-Weller plot
- Excited state electron transfer
- Marcus Theory
- Closs experiment
- Photoredox catalysis
- Transition metal complexes as photocatalysts
- Replacing expensive TM complexes with dyes
- Sacrificial electron donors: the case of amines



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(Heterogeneous) photocatalysis

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Improving Photoredox Catalysis



- Start with expensive transition metal catalysts
- Move to cheaper organic dyes
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- Achieve easy separation/recovery
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Recovery \neq Reuse



Advantages and disadvantages of colloids

Is it homogeneous or heterogeneous?

- From a mechanistic point of view, colloid catalysis is an heterogeneous process taking place on a surface
- From handling and separation aspects a colloid presents similar problems as a homogeneous catalyst, difficult to separate and reuse
- From a mechanistic point of view, colloids are easier than supported nanostructures. Beyond restricting mobility, supports frequently play an active role in the reaction ... that is, they are more than just *supports*.



Heterogeneous vs Homogeneous: conventional classification and its exceptions

Nanocatalysis

Highly reactive superficial sites

Photoredox and photothermal processes

- Non-plasmonic
- Plasmonic NP

Heterogeneous Photoredox catalysis

- TiO₂ as catalyst
- Action spectrum
- Metal-decorated semiconductors

Heterogeneous catalysis



Catalyst supports... beyond immobilization

- A colloidal catalyst may have the properties, including large surface, to catalyze a desirable reaction, but in general they are difficult to separate at the end of the reaction.
- A supported catalyst is frequently easy to separate and reuse
- The “support” generally modifies the catalyst beyond immobilization and easy separation and becomes an integral part of the catalyst, e.g.
 - Adding semiconductor properties
 - Facilitating bringing reactants together
 - Providing acid or base sites

Reduced mobility is a
general property
conferred by supports



Quantum dots

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Quantum dots



- **Materials dimensions**
- **Particle confinement and optical properties**
- **Synthesis**
- **Passivation of QDs**
- **Core-shell QDs**
 - Classification
- **Role of the ligand**
- **Applications**
 - Sensing
 - Light-responsive hybrid material
 - Optoelectronics: QLEDs



Solar energy approaches to energy supply and water quality

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Solar energy?



The photochemistry of the future should not however be postponed to such distant times; I believe that industry will do well in using from this very day all the energies that nature puts at its disposal. So far, human civilization has made use almost exclusively of **fossil solar energy**.

Would it not be advantageous to make better use of radiant energy ?

G. Ciamician. Science 36, 385–394 (1912)



Renewable energy and water decontamination



- 17 Global Goals for Sustainable Development
- TiO_2 and water cleaning
- Solar energy
 - Solar thermal
 - Solar photovoltaic
 - Functioning of a solar cell
 - Dye-sensitized nanocrystalline solar cells: Grätzel cell
- Water splitting and decontamination



Perovskites

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Perovskites (PVK)



- Introduction to PVKs
- Classification
- Synthesis
 - Thin films
 - Solution-based deposition method
 - Vapor deposition
 - Nanocrystals
 - Templated method
 - Non-templated method: hot-injection method vs ligand assisted precipitation
- Ligands
- Tuning optical properties
- Strategies to improve LHP stability
- Applications
 - Solar cells
 - PeLEDs



Overall



Simple tunability of the band gap energy (E_g).

The bottom of the conduction band of hybrid perovskite is mainly formed by the p orbitals of the Pb atoms, while the valence band maximum is mainly composed by the p orbitals of the halide

Low exciton binding energy.

This feature implies spontaneous and efficient charge separation at room temperature,

Large absorption coefficient.

The strong light absorption

Long-range diffusion length and high carrier mobilities.

Inexpensive precursor materials and simple synthesis