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

Prof. Juan Scaiano; Prof. Tebello Nyokong; Dr. Anabel Lanterna;

© 2019, JUAN SCAIANO, TEBELLO NYOKONG, ANABEL LANTERNA

This work is licensed under the Creative Commons Attribution License (https://creativecommons.org/licenses/by/4.0/legalcode), which permits unrestricted use, distribution, and reproduction, provided the original work is properly credited.

Cette œuvre est mise à disposition selon les termes de la licence Creative Commons Attribution (https://creativecommons.org/licenses/by/4.0/legalcode), qui permet l’utilisation, la distribution et la reproduction sans restriction, pourvu que le mérite de la création originale soit adéquatement reconnu.

IDRC Grant/ Subvention du CRDI: 108569-001-Canada-South Africa trilateral research chair in nanomaterials for clean water
Light-matter interactions

Development of smart photoactive materials for environmental applications
Semiconductors and fluorescent nanomaterials

J.C. (Tito) Scaiano
jscaiano@uottawa.ca
Band theory of solids: molecules vs semiconductors

- LUMO
  - Light
  - Available: 2 electrons in orbital

- HOMO
  - Light

- Conduction band (CB)
  - e−

- Valence band (VB)
  - h⁺

- Light-matter interactions
Semiconductor properties and applications

- Electroluminescence from semiconductors
- Conductivity
- Doping: n-doped and p-doped semiconductors. Diodes.

- TiO₂: 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
Introduction to Photochemistry

J. C. (Tito) Scaiano
jscaiano@uottawa.ca
**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**

- **UV**
- **Visible region**
- **NIR & IR**

More energy, bonds break

Less energy, bonds vibrate
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

Anabel E. Lanterna
alatern@uottawa.ca
Excited state complexes

Two identical molecules:

**EXCI**ted di**MER** → EXCIM**ER**

Two different molecules:

**EXCI**ted com**PLEX** → EXCIP**LEX**
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
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.

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

with more concepts on electron transfer

J.C. (Tito) Scaiano

jscaiano@uottawa.ca
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

Excited state of naphthalene returns enough energy to make it possible
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 $\text{Ru(bpy)}_3^{+2}$ and $\text{EtNiPr}_2$
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
(Heterogeneous) photocatalysis

Anabel E. Lanterna
alantern@uottawa.ca
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

Recovery ≠ Reuse
Advantages and disadvantages of colloids

- 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 photocatalysis

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
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

Anabel E. Lanterna
alantern@uottawa.ca
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

J.C. (Tito) Scaiano
jscaiano@uottawa.ca
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?


The solar (radiant) energy received by Earth one hour exceeds the world energy usage in one year
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

Anabel E. Lanterna
alantern@uottawa.ca
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.