Aalto University
School of Chemical
Engineering

Functional Inorganic Materials
Lecture 11:
Luminescent and optically active materials

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Lecture Exercise 11 is a MyCourses Quiz

Contents

- General overview of luminescence
- Electroluminescence
  - Light-emitting diodes
- Photoluminescence
  - Jablonski diagrams
  - Organic light-emitting diodes (OLED)

Figure: Wikimedia Commons / PiccoloNamek (CC BY-SA)

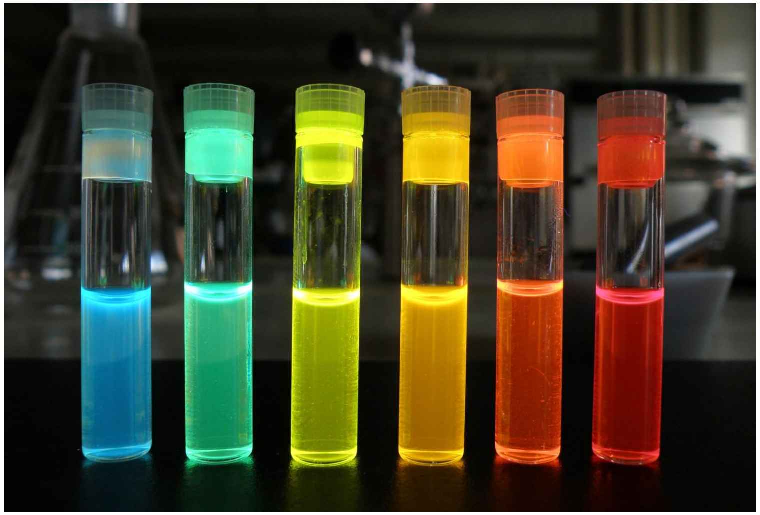


Figure: Igor Koshevoy / UEF

Electromagnetic spectrum visible to the human eye

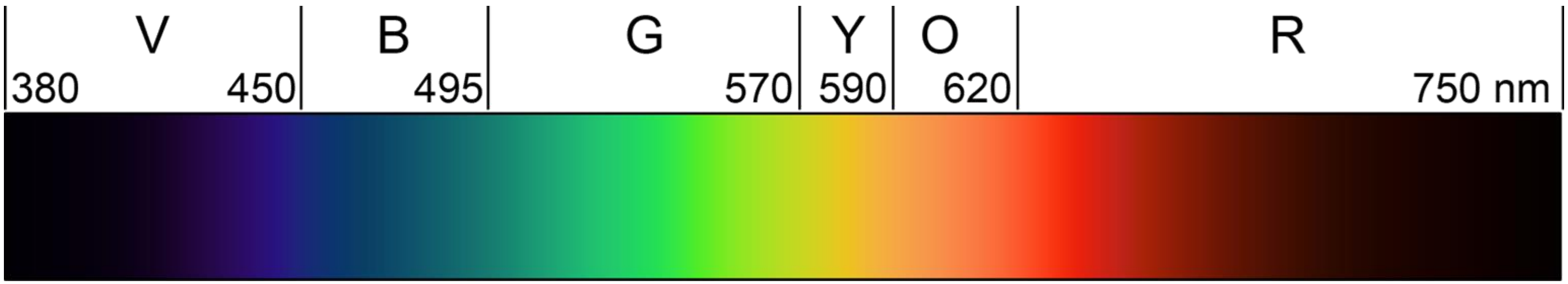


Figure: Wikimedia Commons (Public Domain)

Color	Wavelength (nm)	Frequency (THz)	Photon energy (eV)
violet	380–450	670–790	2.75–3.26
blue	450–485	620–670	2.56–2.75
cyan	485–500	600–620	2.48–2.56
green	500–565	530–600	2.19–2.48
yellow	565–590	510–530	2.10–2.19
orange	590–625	480–510	1.98–2.10
red	625–750	400–480	1.65–1.98

Luminescence

- IUPAC definition of luminescence:
  - Spontaneous emission of radiation from an electronically or vibrationally excited species not in thermal equilibrium with its environment.

- **Electroluminescence:** resulting from electric current passed through a substance.
- **Photoluminescence**, a result of absorption of photons.
  - Fluorescence: photoluminescence from singlet–singlet electronic relaxation.
  - Phosphorescence: photoluminescence either from triplet–triplet electronic relaxation or persistent luminescence (typical lifetime: microseconds to hours)
- **Chemiluminescence**, the emission of light as a result of a chemical reaction.
  - Bioluminescence, a result of biochemical reactions in a living organism.
  - Electrochemiluminescence, a result of an electrochemical reaction.
- **Mechanoluminescence**, a result of a mechanical action on a solid.
  - Triboluminescence: generated when material is scratched, crushed, or rubbed.
  - Piezoluminescence: produced by the action of pressure on certain solids.

Source: https://en.wikipedia.org/wiki/Luminescence

Electroluminescence

Figure: Wikimedia Commons / PiccoloNamek (CC BY-SA)

Electroluminescence

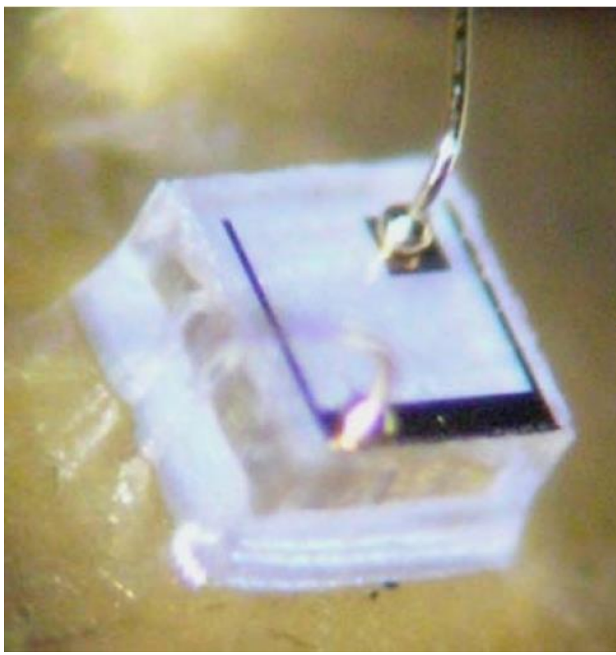
- Electroluminescence arises when an electric current passes through a material.
- Typical application: Light-Emitting Diode (LED)
  - Typically based on a semiconductor material.
  - A device working in the opposite direction (electricity from photons) is called a **photodiode**.
  - Solar cells working in photovoltaic mode are examples of photodiodes.

- Let's focus on LEDs and LED materials as examples of electroluminescence.
- Examples from the work of Shuji Nakamura, one of the recipients of 2014 Nobel Prize in Physics.
  - "For the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources" (with Isamu Akasaki and Hiroshi Amano)
  - https://www.nobelprize.org/prizes/physics/2014/nakamura/facts/

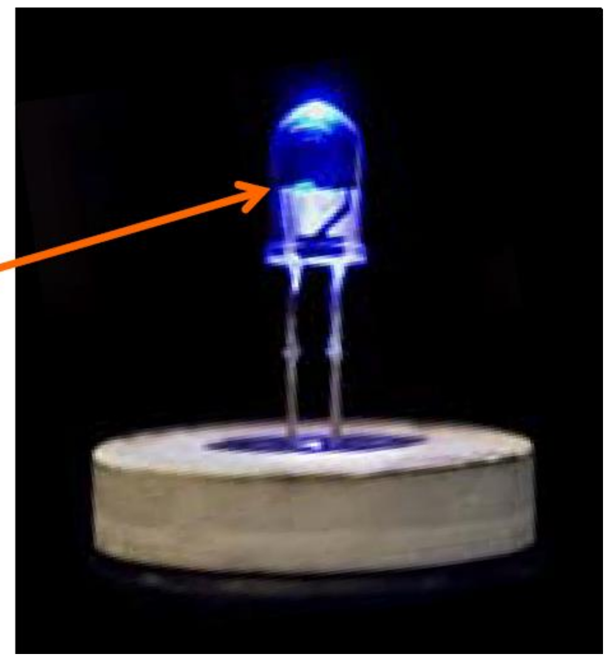
Light-Emitting Diode (1/2)

- Light-Emitting Diode (LED) produces light of a single color by combining holes and electrons in a semiconductor.

Actual blue LED
(size: 0.4 mm × 0.4 mm)



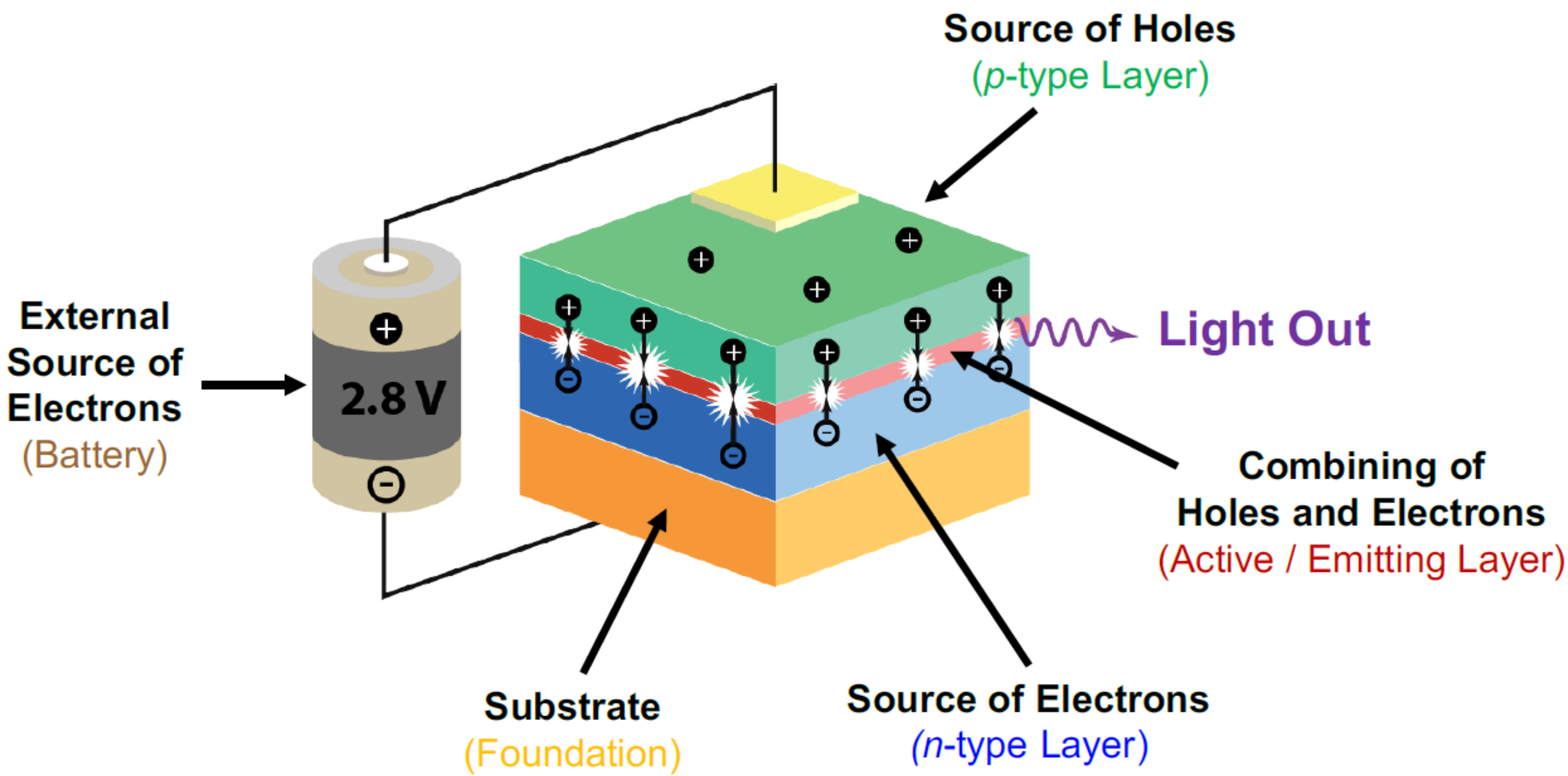
Packaged blue LED



Source: Nobel lecture of Shuji Nakamura

Light-Emitting Diode (2/2)

- Light-Emitting Diode (LED) produces light of a single color by combining holes and electrons in a semiconductor.



Source: Nobel lecture of Shuji Nakamura

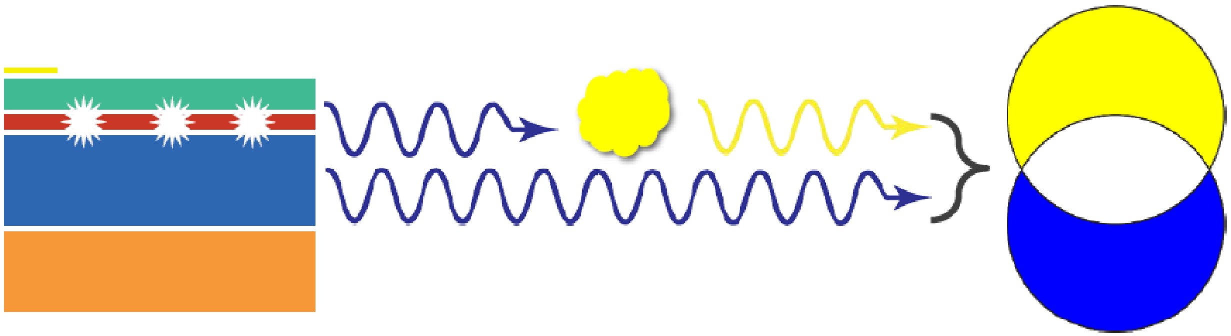
White LED

- White LEDs work by combining blue light with other colors (red, yellow, green)
- For example, convert blue LED light to yellow using a **phosphor** material.

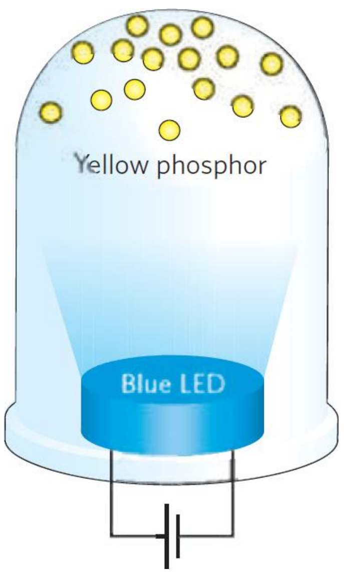
Blue LED

Phosphor converts blue → yellow

White light = blue + yellow



White LED



Source: Nobel lecture of Shuji Nakamura & S. Pimputkar et al., *Nature Photonics* **3** (2009) 180—182.

Blue LED material: Indium Gallium Nitride (InGaN)

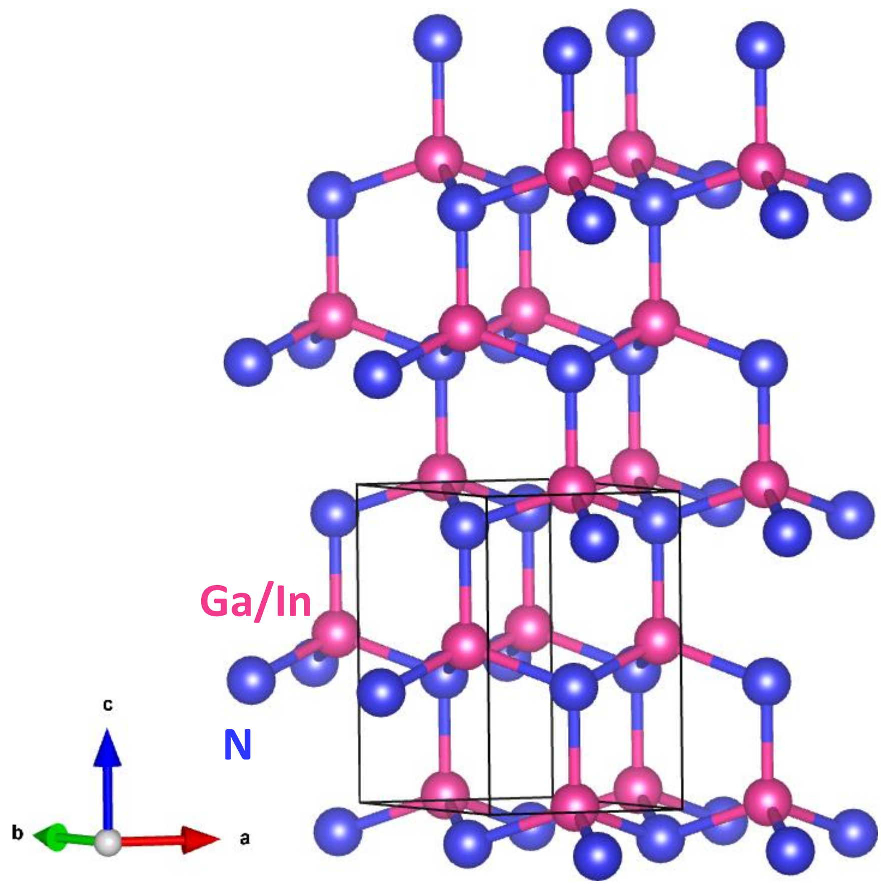


Figure: AJK

GaN (space group $P6_3mc$)
Wurtzite structure type (same as ZnO)

Indium Gallium Nitride = $In_xGa_{1-x}N$

<u>Wavelength vs. Indium Fraction</u>

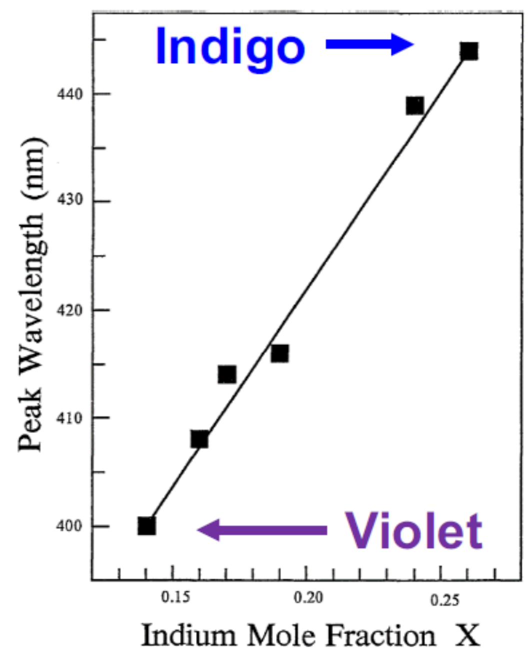


Figure: Nobel lecture of Shuji Nakamura.

Example of a phosphor material

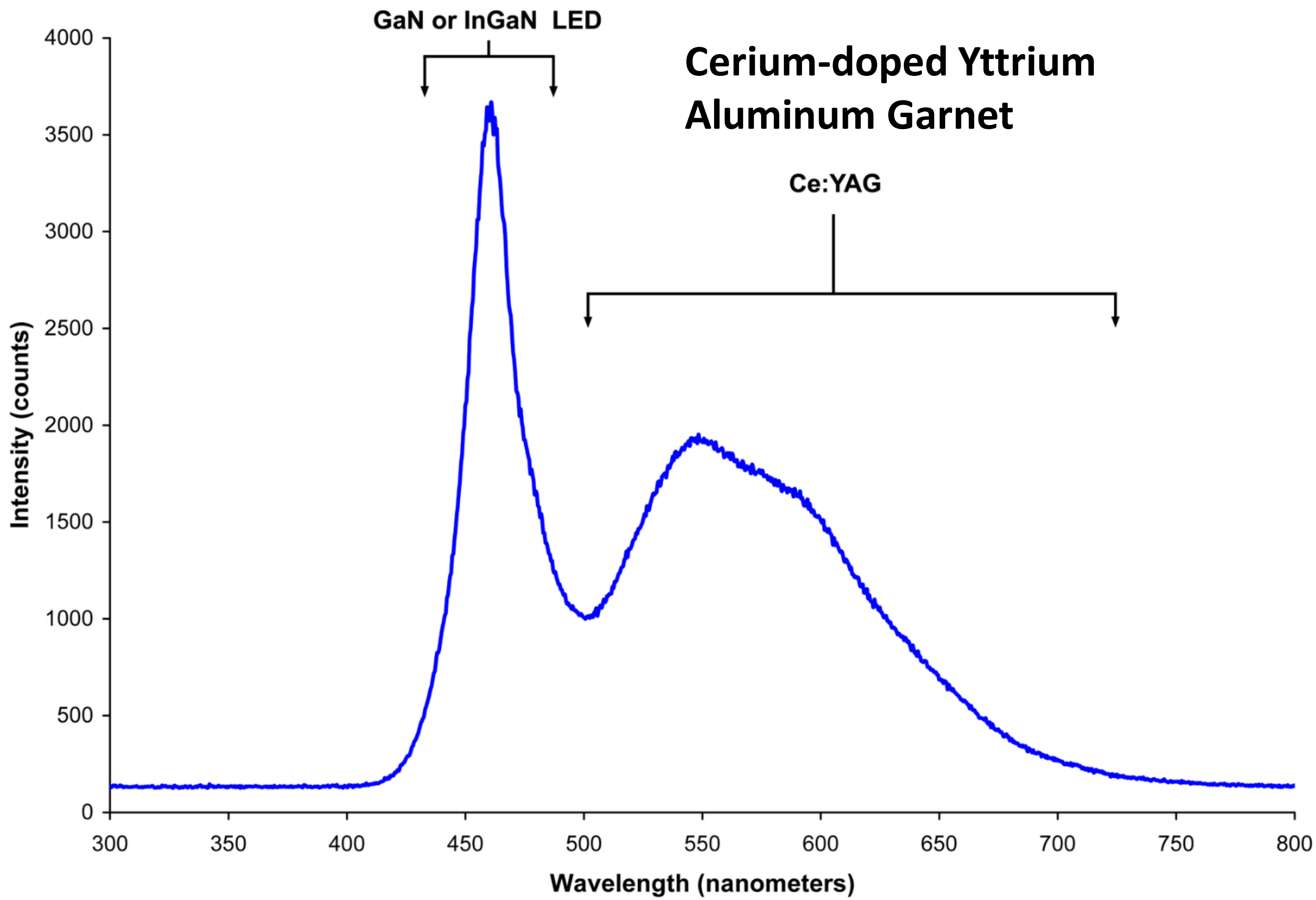
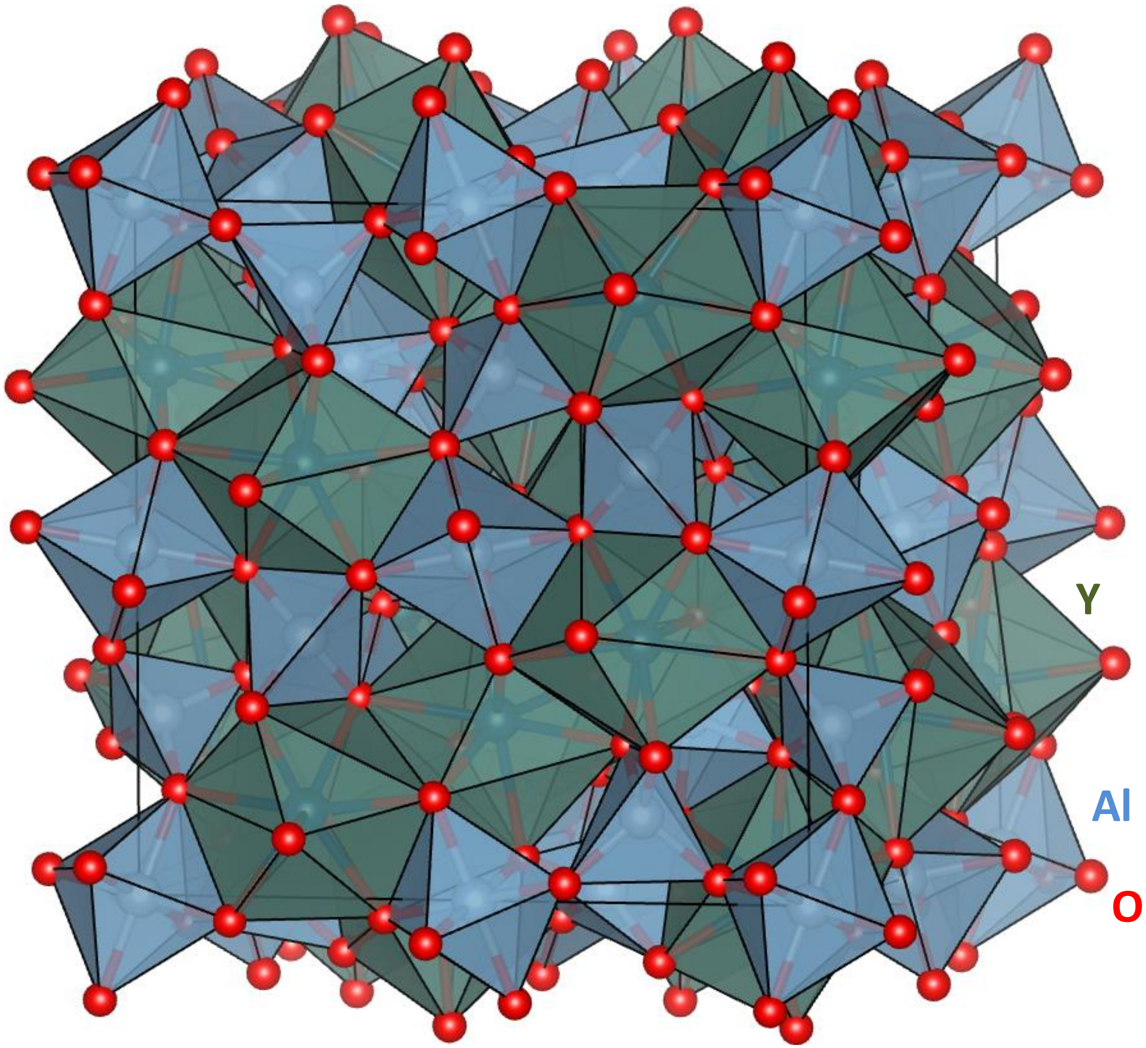


Figure: Wikimedia Commons / Deglr6328

Cerium-doped Yttrium Aluminum Garnet



Ce:YAG

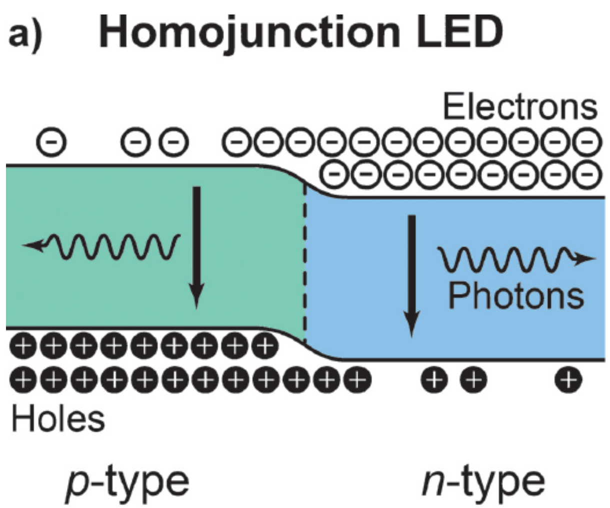
YAG = $Y_3Al_5O_{12}$

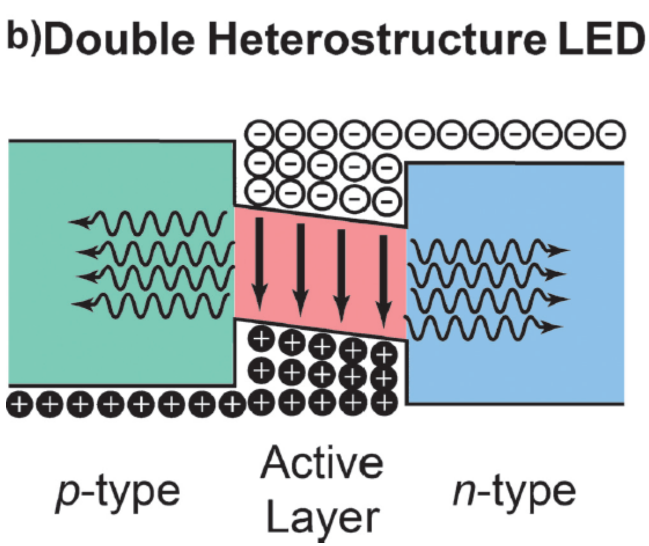
Space group *Ia*-3*d*

Y(III) has 8-fold coordination (dodecahedral coordination polyhedron)

Al(III) has octahedral and tetrahedral sites in ratio 2:3.

Double heterostructure LED (1/2)

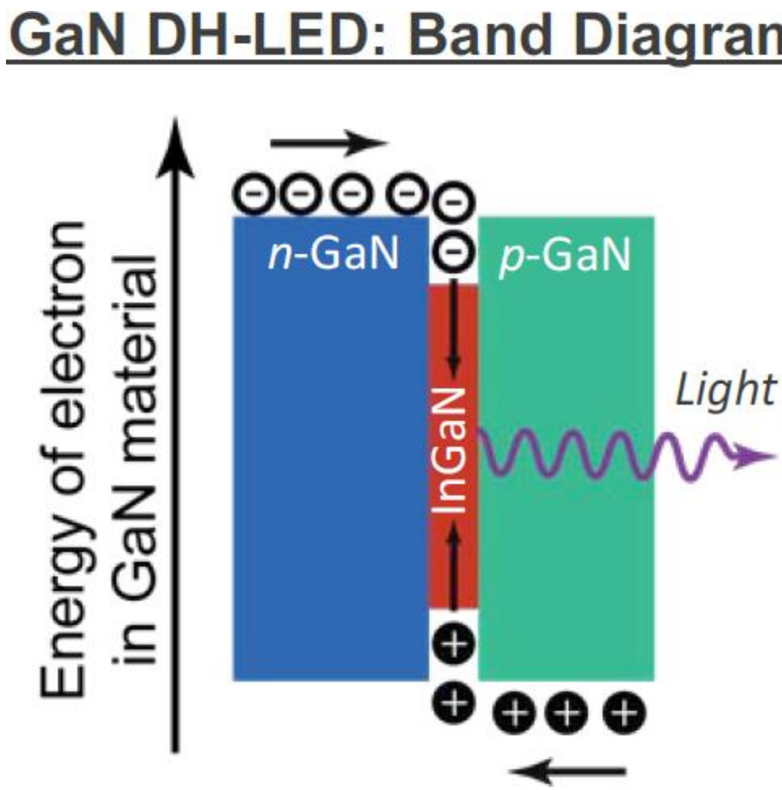


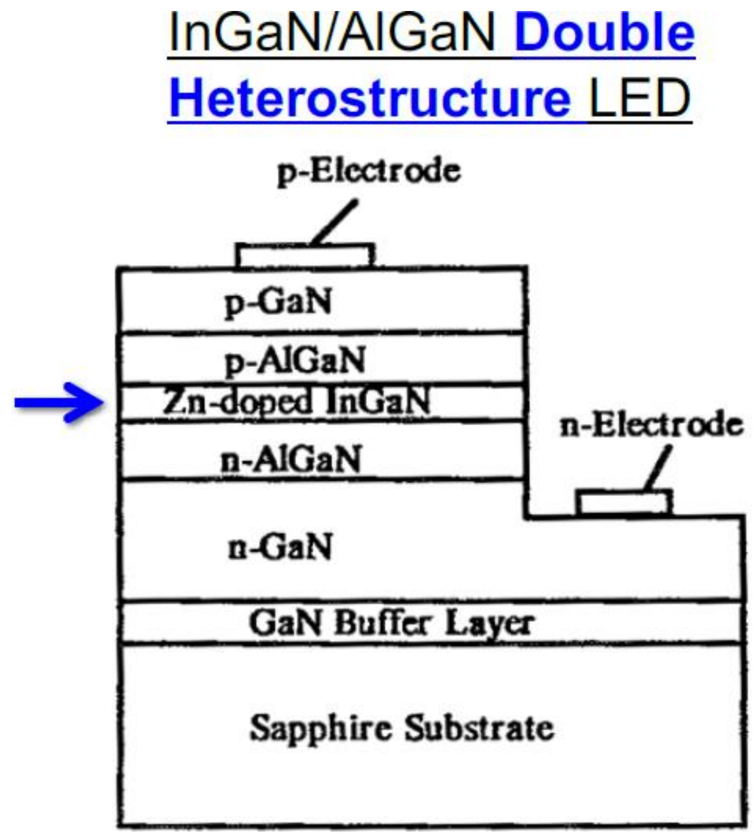


- Double heterostructures increase carrier concentration in the active layer
- Enhanced radiative recombination rates (more light generated) compared to homojunction LED.

Source: Nobel lecture of Shuji Nakamura

Double heterostructure blue LED





Fabrication with MOCVD (Metal-Organic Chemical Vapor Deposition

Source: Nobel lecture of Shuji Nakamura

Applications for LEDs


Solid State Lighting


Decorative Lighting


Automobile Lighting

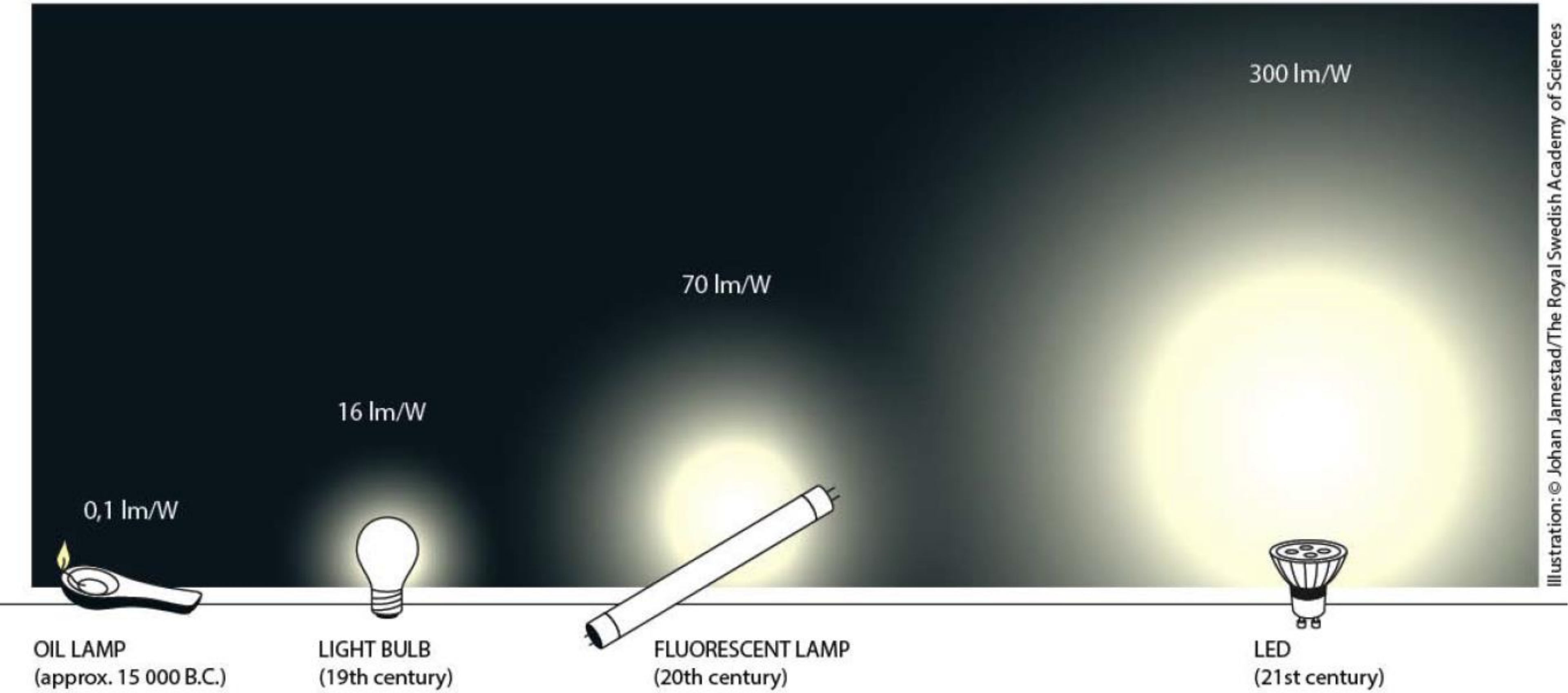

Displays


Agriculture


Indoor Lighting

Source: Nobel lecture of Shuji Nakamura.

Energy saving with LEDs



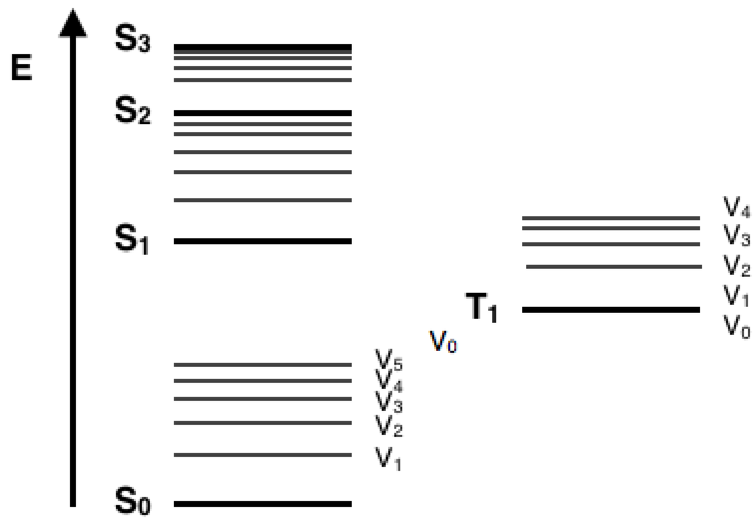
Sources: www.nobelprize.org, US Department of Energy

- ~ 40 % electricity savings (261 TWh) in USA in 2030 thanks to LEDs
- Eliminates the need for 30+ 1000 MW power plants by 2030

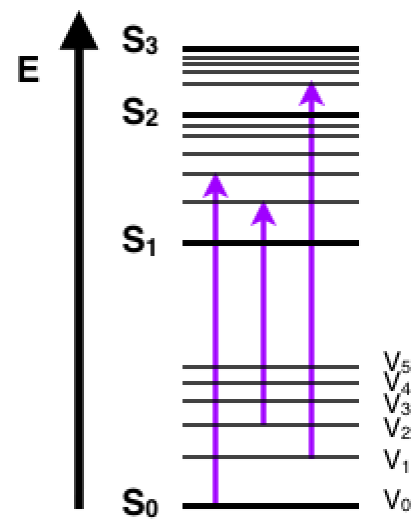
Photoluminescence

Organometallic light-emitting complexes from Igor Koshevoy (University of Eastern Finland)

Jablonski diagrams (1/3)



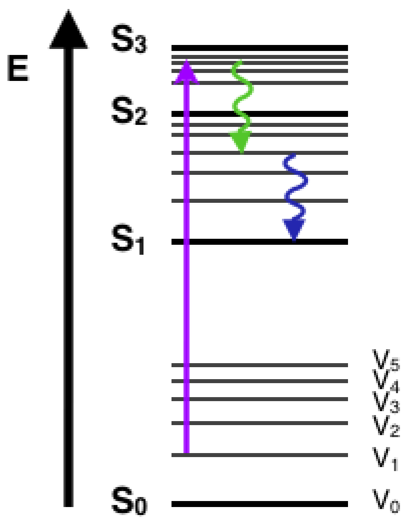
Foundation of a typical Jablonski Diagram

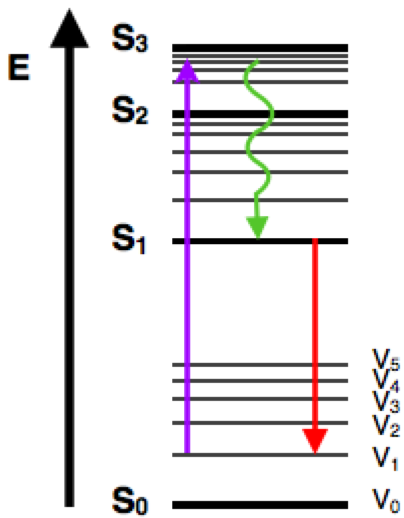


Three possible absorption transitions represented.

Source: chem.libretexts.org (CC BY)

Jablonski diagrams (2/3)

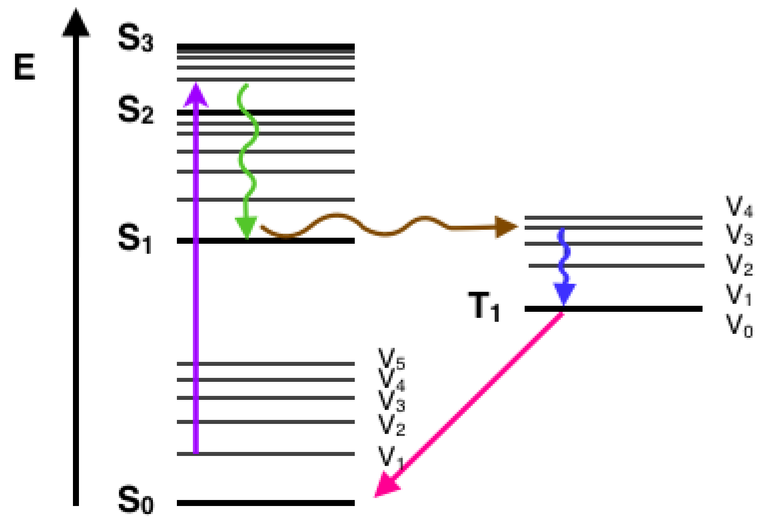




Possible scenario with absorption, internal conversion, and vibrational relaxation *processes shown.*

Possible scenario with absorption, internal conversion and vibrational relaxation, and fluorescence processes shown.

Jablonski diagrams (3/3)

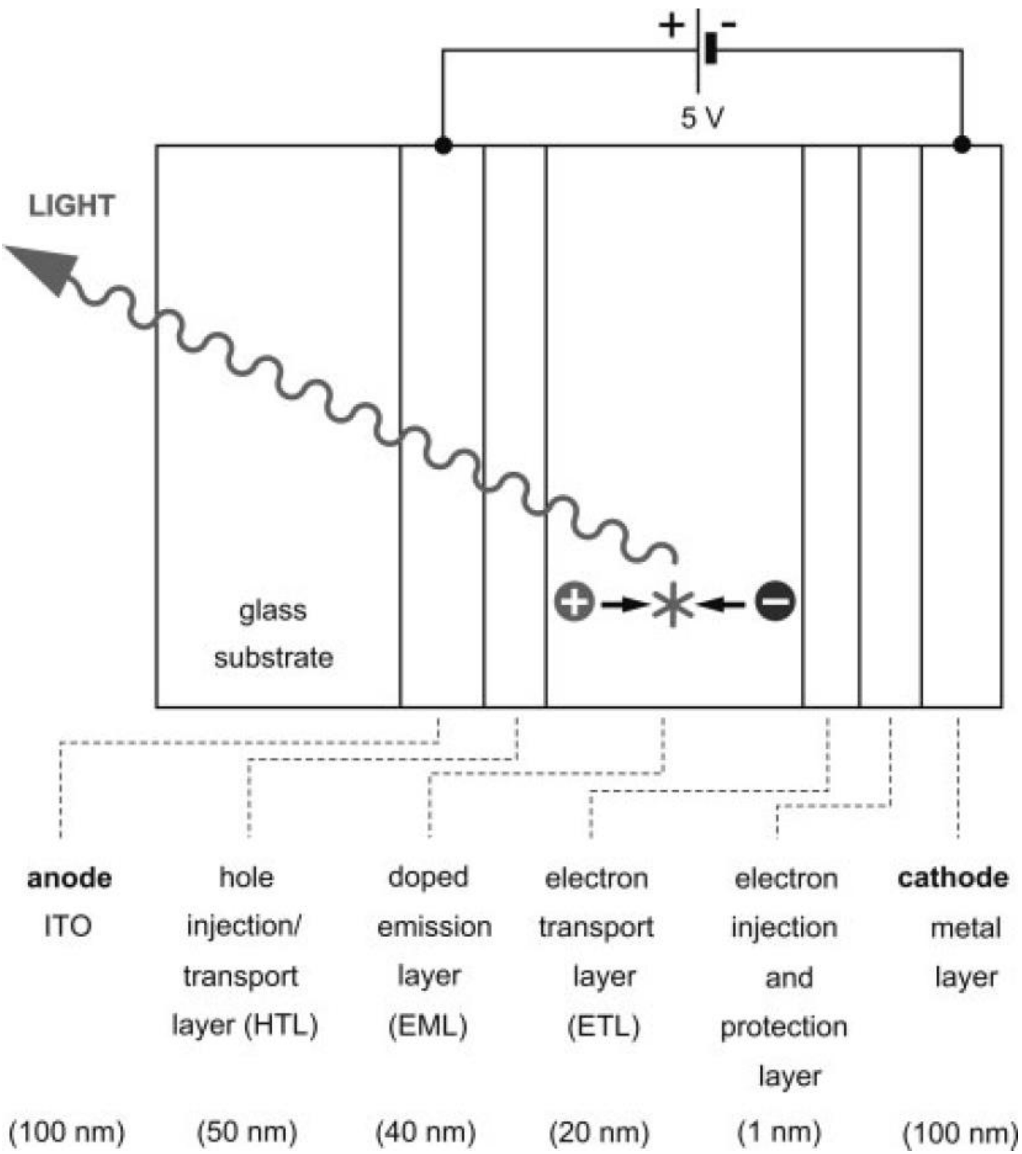


Possible scenario with absorption, internal conversion, vibrational relaxation, intersystem crossing, and phosphorescence processes shown.

Timescales

Transition	Timescale	Radiative Process?
Internal Conversion	10^{-14} - 10^{-11} s	no
Vibrational Relaxation	10^{-14} - 10^{-11} s	no
Absorption	10^{-15} s	yes
Phosphorescence	10^{-4} - 10^{-1} s	yes
Intersystem Crossing	10^{-8} - 10^{-3} s	no
Fluorescence	10^{-9} - 10^{-7} s	yes

Organic light-emitting diode (1/2)



Basic set - up of an organic light - emitting diode (OLED).

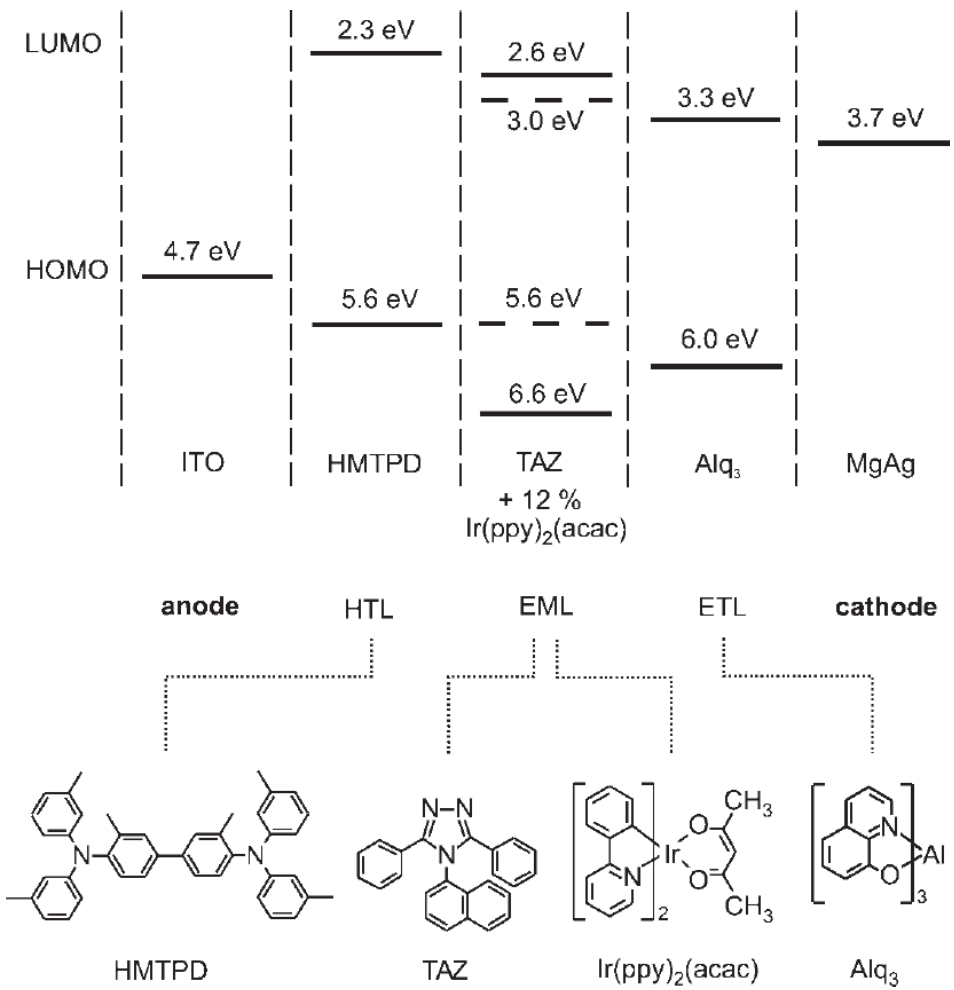
The different layers are not drawn to scale. Examples of materials used for a realization of an OLED device are given on the next slide.

The key process is the electron(−) – hole(+) recombination (*).

Optimized commercial OLEDs contain additional hole and/or electron blocking layers.

Figure: Yersin 2007

Organic light-emitting diode (1/2)



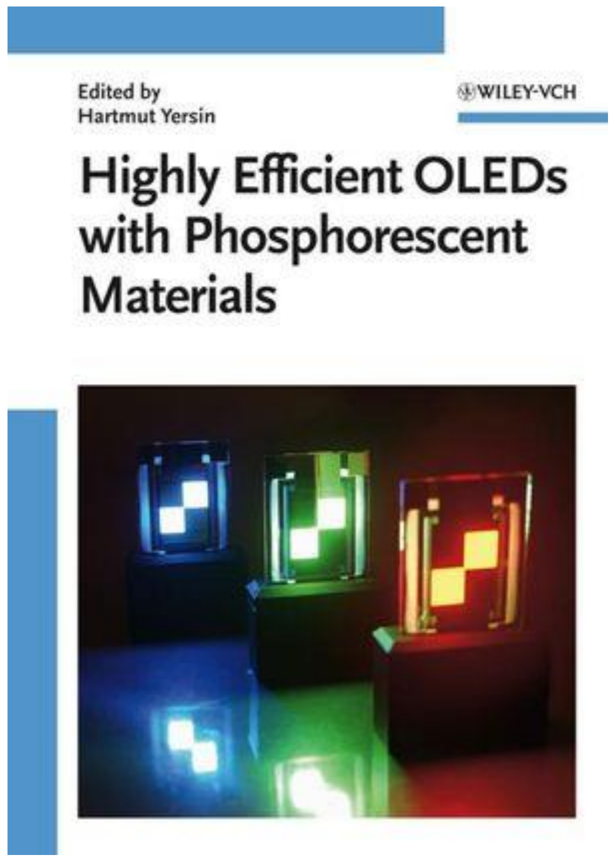
HOMO - LUMO diagram and materials of an OLED device similar to previous slide.

The HOMO/LUMO values are given relative to the vacuum level.

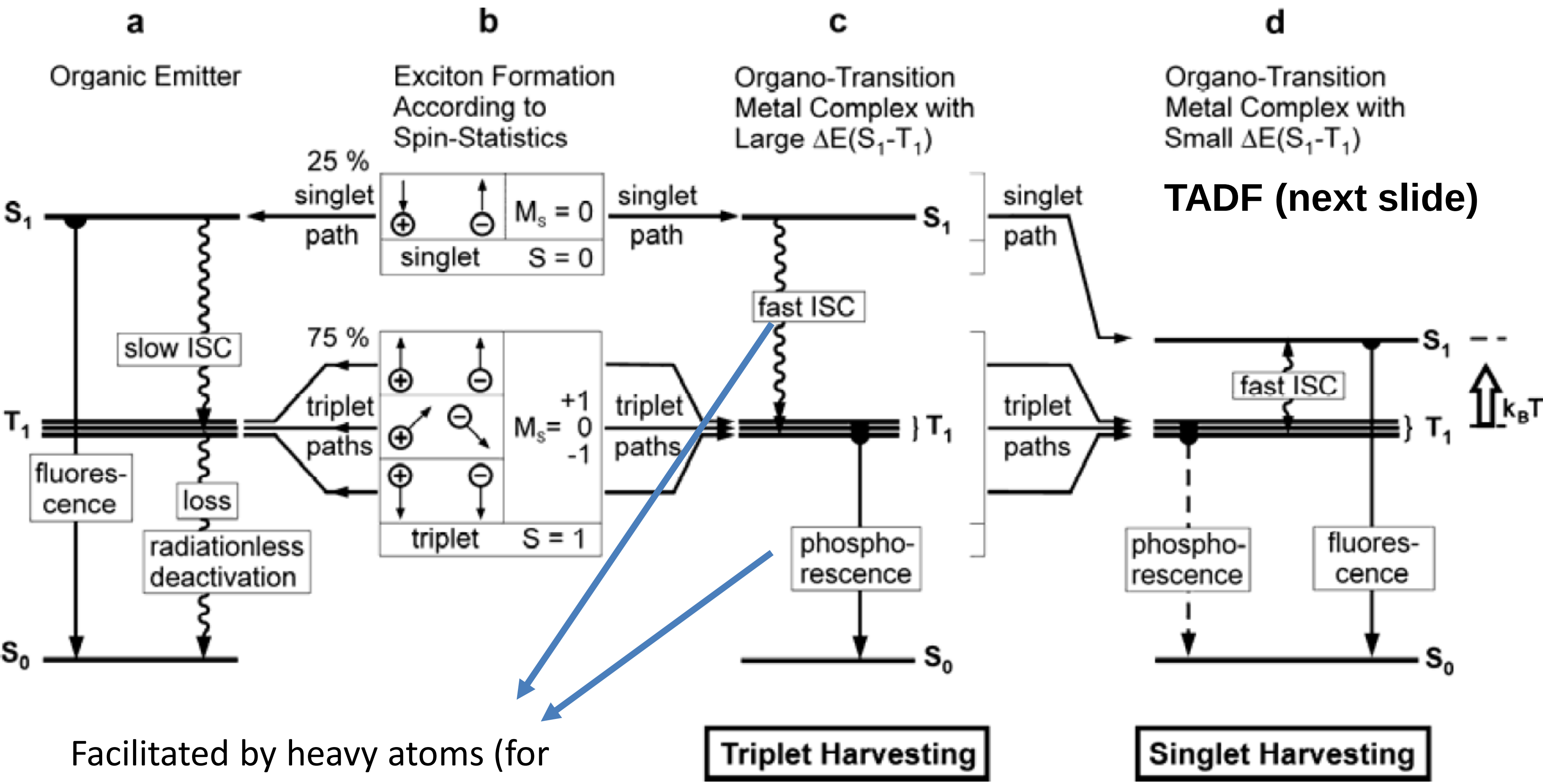
For the emission layer (EML), the oxidation and reduction potentials are given for the host (TAZ, solid line) and the emitter (Ir(ppy) 2 (acac), dashed line).

Figure: Yersin 2007

Phosphorescent OLEDs (PhOLED)



Organometallic emitters



Facilitated by heavy atoms (for example, Au). Spin-orbit coupling and relativistic effects!

Longer lifetime (not necessarily good for applications)

Thermally Assisted Delayed Fluorescence

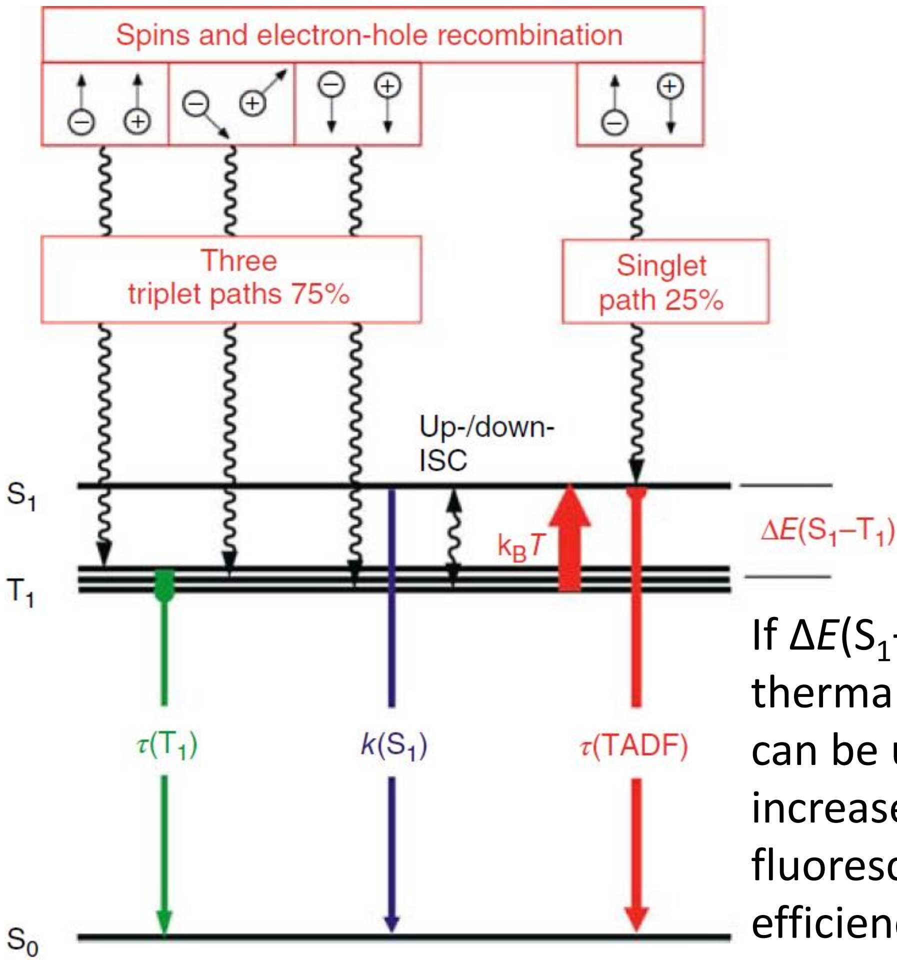
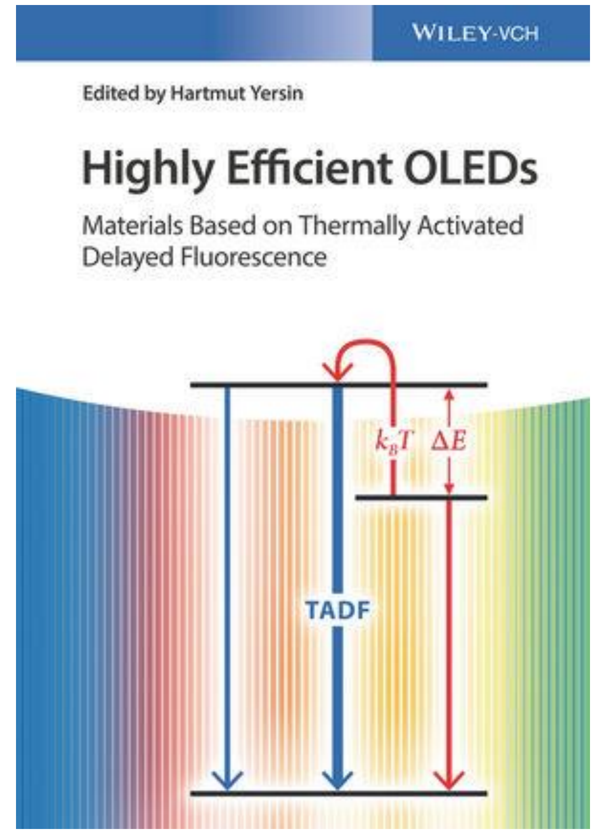


Figure 1.1 Illustration of the molecular TADF effect and its use in OLEDs (singlet harvesting). $\tau(T_1)$ and τ(TADF) are the phosphorescence decay time and the TADF decay time, respectively. $k(S_1) = k_r(S_1 \rightarrow S_0)$ is the radiative rate of the $S_1 \rightarrow S_0$ transition (prompt fluorescence). Up-ISC is also often denoted as reverse intersystem crossing (rISC).

If $\Delta E(S_1–T_1)$ is small, thermal excitations can be used to increase the fluorescence efficiency.



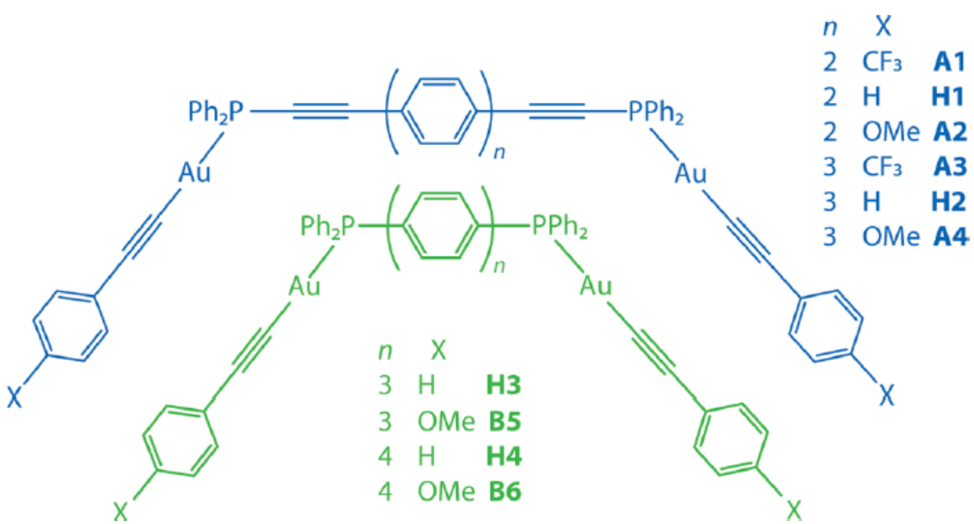
More details on spin statistics

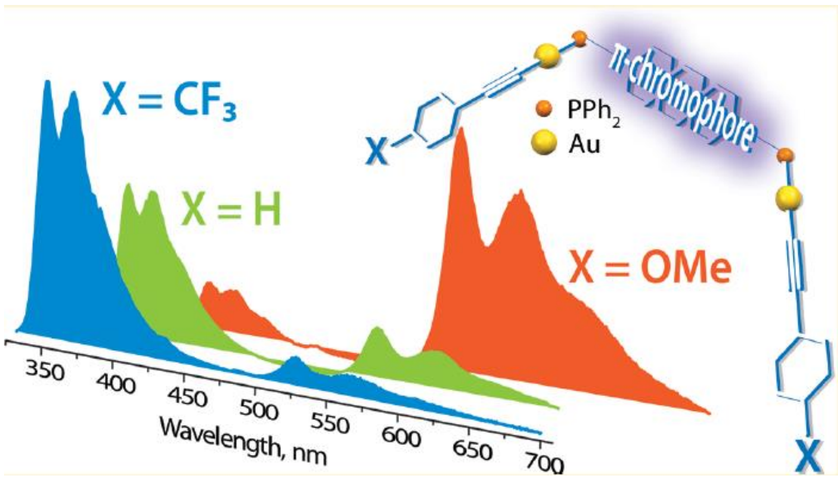
Understanding electronic transitions with DFT (1/2)

Harnessing Fluorescence versus Phosphorescence Ratio via Ancillary Ligand Fine-Tuned MLCT Contribution

Ilya Kondrasenko,[†] Kun-you Chung,[‡] Yi-Ting Chen,[‡] Juha Koivistoinen,[§] Elena V. Grachova,[||] Antti J. Karttunen,[*,⊥] Pi-Tai Chou,[*,‡] and Igor O. Koshevoy[*,†]

Scheme 1. Structures of complexes A1–A4, B5, B6, and H1–H4





Understanding electronic transitions with DFT (2/2)

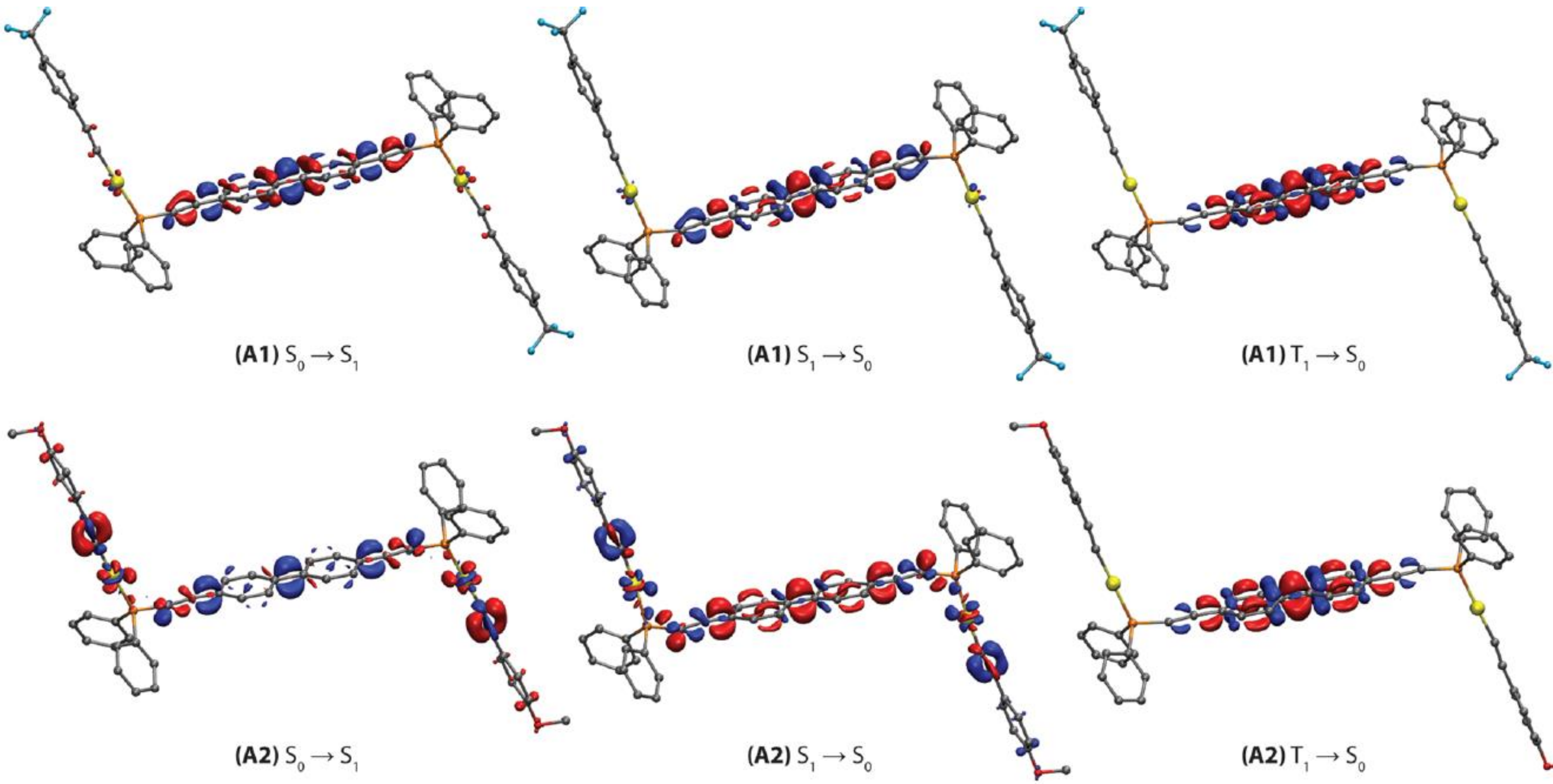


Figure 3. Electron density difference plots for the lowest energy singlet excitation ($S_0 \rightarrow S_1$), singlet emission ($S_1 \rightarrow S_0$), and triplet emission ($T_1 \rightarrow S_0$) of the complexes **A1** and **A2** (isovalue 0.002 au). During the electronic transition, the electron density increases in the blue areas and decreases in the red areas. Hydrogen atoms omitted for clarity.

Electron densities from Density Functional Theory (DFT)

J. Phys. Chem. C **2016**, *120*, 12196–12206. DOI: [10.1021/acs.jpcc.6b03064](https://doi.org/10.1021/acs.jpcc.6b03064)