

ELEC-E9210 Organic Electronics: Materials,  
Devices & Applications

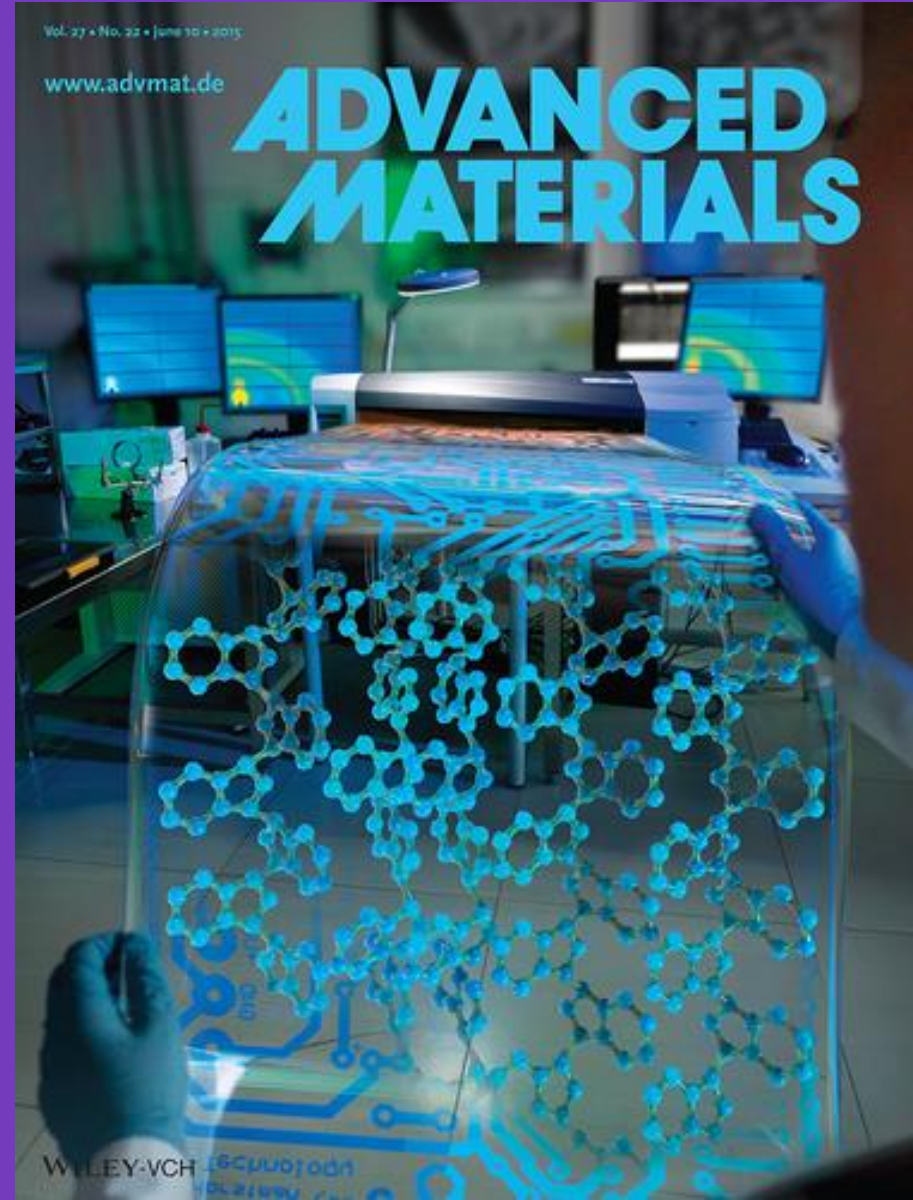
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# Optical Excitation in Organic Materials

A<sup>”</sup>

Aalto University  
School of Electrical  
Engineering

<https://organicelectronics.aalto.fi>



# From Last Class

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## Previously....

- What are Organic Materials (primarily composed of **carbon**, **hydrogen** and **oxygen** held together by **van der Waals forces**)
- **Small molecules** or **polymers**, and can transport either  $h^+$  or  $e^-$ , often both
- **Different morphologies** can be found for same organic materials, depending on molecular packing, fabrication process and condition, with an overall effect on **functional properties**
  
- **Electronic properties** and **different transport mechanisms** in OSC (doping, trapping effect, field-effect transport)

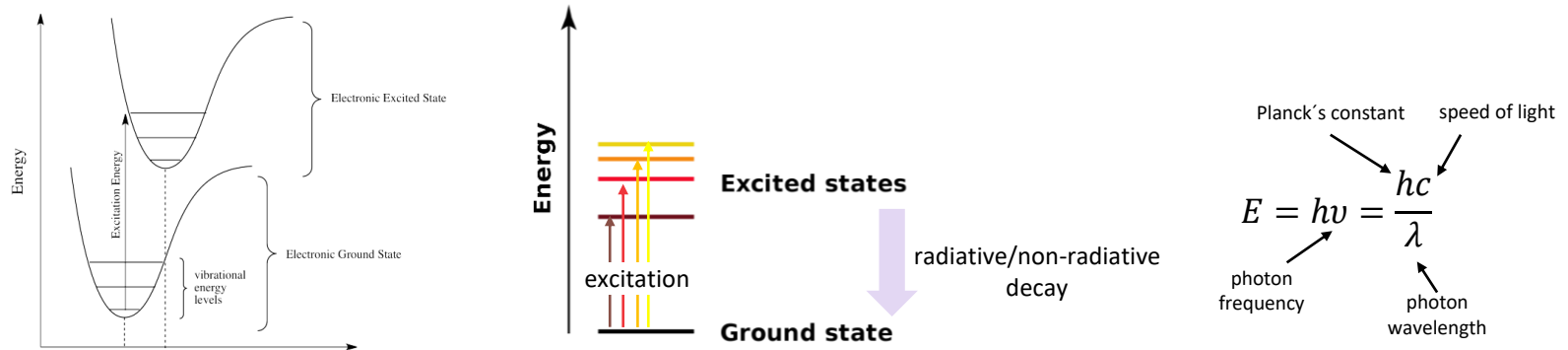
## Today's Class

- **Optical excitation** in OSC (optical transitions, light emission mechanism, excitons, etc. )

# Optical Excitation of OSC

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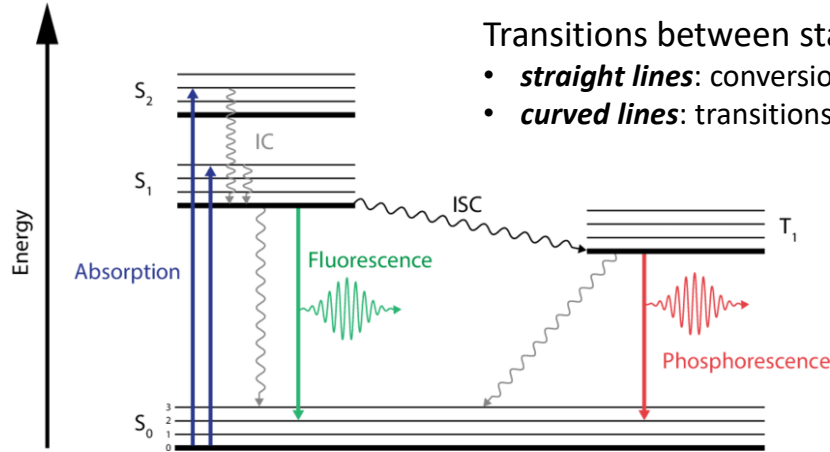
An organic molecule (similar to inorganic counterpart) can be excited to its electronic excited state



**optical excitation** (energy > energy gap of the molecule):

- *molecule absorbs a photon, promoting the molecule to an excited state*  
→ molecule returns to its ground state through *radiative/non-radiative decay*
- different molecules will absorb different frequencies of light, depending on electronic and vibration structure

# Jablonski Diagram



Transitions between states occur in the molecule upon optical excitation

- **straight lines:** conversion between a photon and an electron
- **curved lines:** transitions of electrons without light interaction

**ABSORPTION:** *electron is excited from a lower energy level to a higher energy level*

with energy transferred from photon to the electron.

- allowed  $\lambda$  = energy difference between the levels
- timescale :  $10^{-15}$ s

**INTERNAL CONVERSION (IC):** *radiation-less transition between states with the same spin state*

- timescale:  $10^{-14}$ - $10^{-11}$ s

**FLUORESCENCE:** *electron in excited states (singlet) decays to a lower energy states*

- timescale:  $10^{-9}$ - $10^{-7}$ s

**INTERSYSTEM CROSSING (ISC):** *radiation-less transition between states with different spin state*

- timescale:  $10^{-8}$ - $10^{-3}$ s

**PHOSPHORESCENCE:** *electron in excited states (triplet) decays to a lower energy states*

- timescale:  $10^{-4}$ - $10^{-1}$ s

# Absorption in Organic Materials

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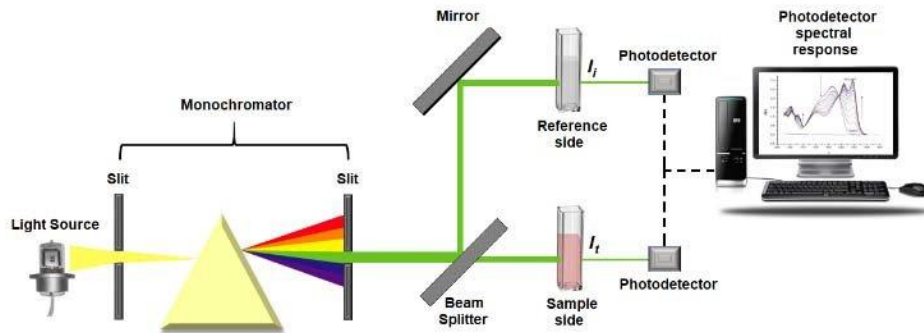
## Beer's Law for Absorption

$$A = \epsilon b C \text{ (solution)}$$

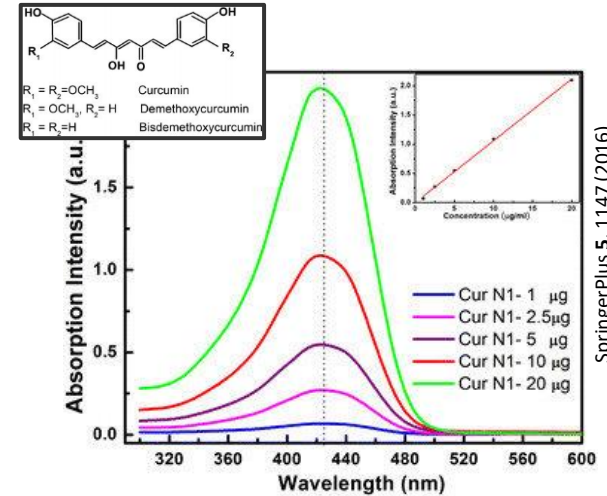
$\epsilon$  = molar attenuation coefficient  
 $b$  = path length  
 $C$  = concentration

$$I = I_0 e^{-\alpha d} \text{ (thin film)}$$

$I_0, I(\lambda)$  incident and absorbed light  
 $\alpha$  = absorption coefficient  
 $d$  = film thickness



Schematics experimental set-up to measure absorption properties

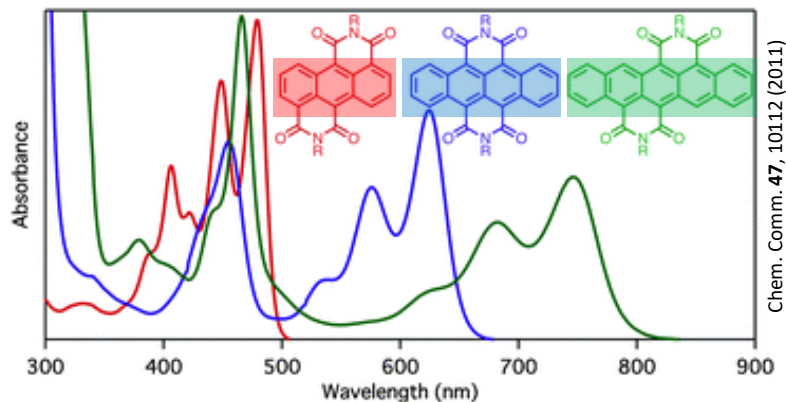


SpringerPlus 5, 1147 (2016)

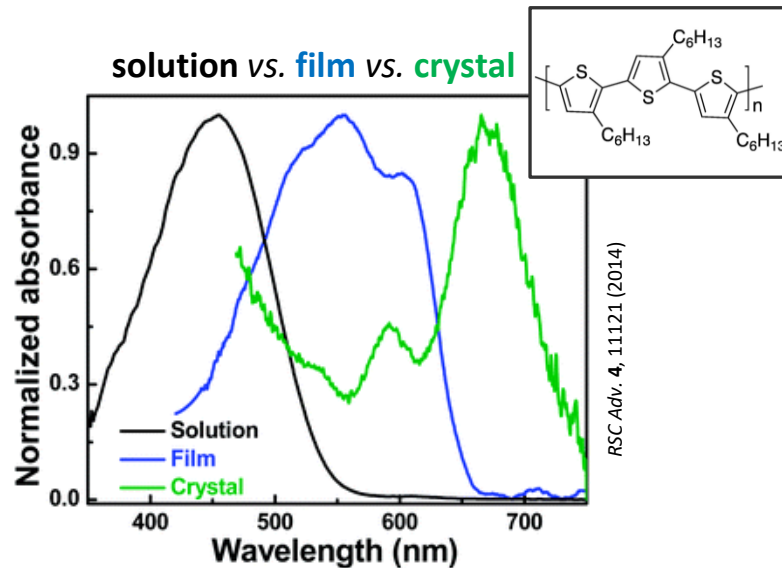
Absorption spectra of curcumin-ethanol solutions for different curcumin concentration. Curcumin solution shows absorbance at  $\lambda=425\text{nm}$  and linear increasing absorption with increasing concentration.

# Absorption in Organic Materials (II)

... as function of different molecules

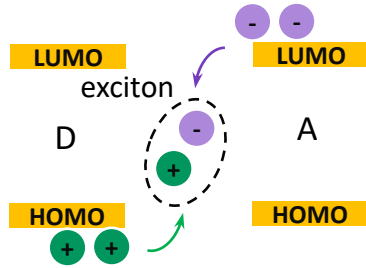


UV-vis absorption of different acene-based molecules  
(anthracene, tetracene, pentacene)



UV-Vis spectra of P3HT in three different forms: **crystal**, solution (in 3-hexyl-thiophene), **thin film** (spin-cast) on glass. Differences arise from **aggregation** (solution), **molecular packing** (thin film) and **crystal structure**

# Excitons: Concept & Properties



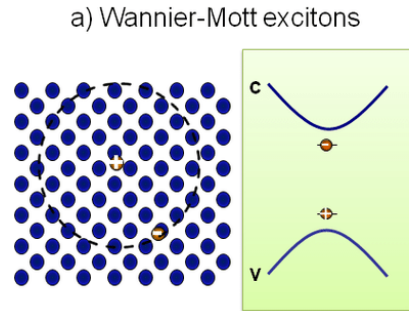
Collective response upon excitation in a molecular crystal can be described in terms of **exciton**, a *quasi-particle formed by an electron and hole bound together by Coulomb forces*.

Upon formation, exciton can move through the material.

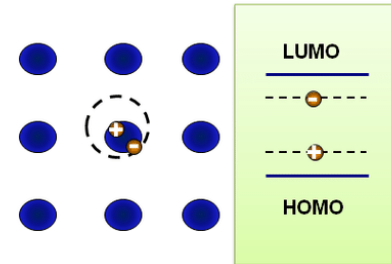
**exciton radius:** average distance between electron and hole

## less localized

- radius  $< 10s \text{ \AA}$
- binding energy ( $< 10\text{meV}$ )
- *band-like* structure



## b) Frenkel excitons



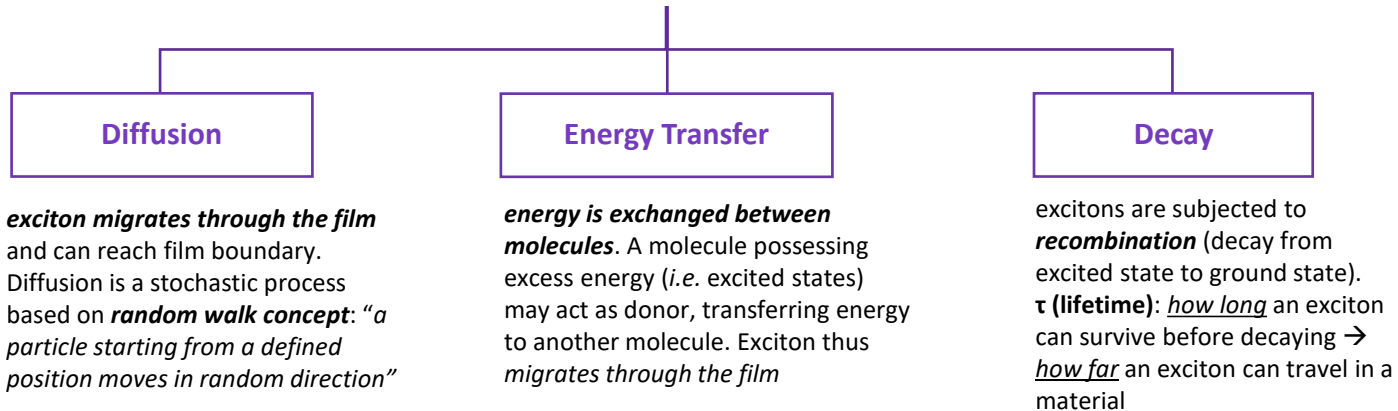
## highly localized

- radius  $< 5\text{\AA}$
- binding energy ( $0.1\text{-}1\text{eV}$ )
- “*flat*” band

# Exciton Dynamics

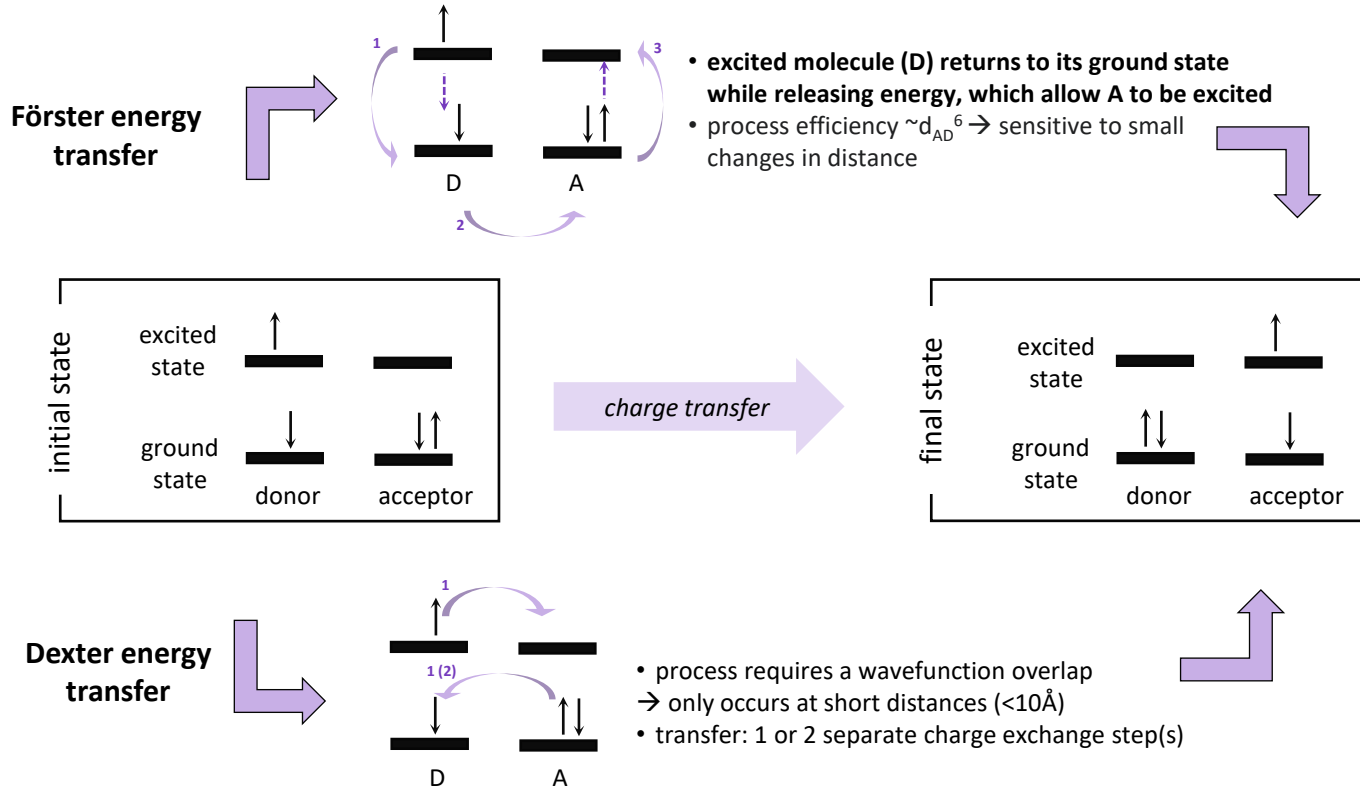
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excitons can move in the material in a coherent way (*wavelike* manner) and it **can decay radiatively** and **non-radiatively**





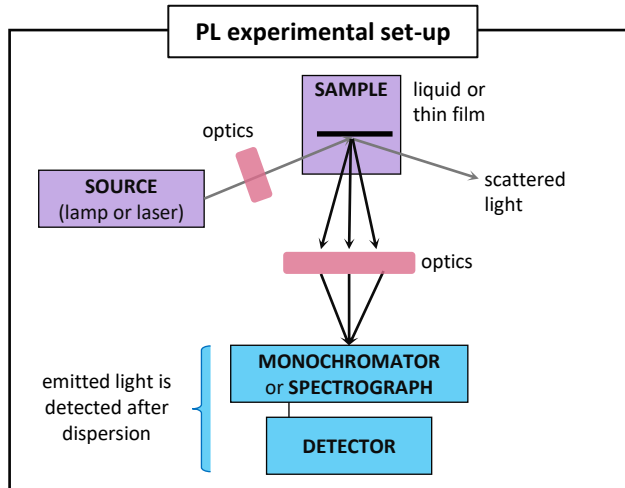
# Excitons: Energy Transfer



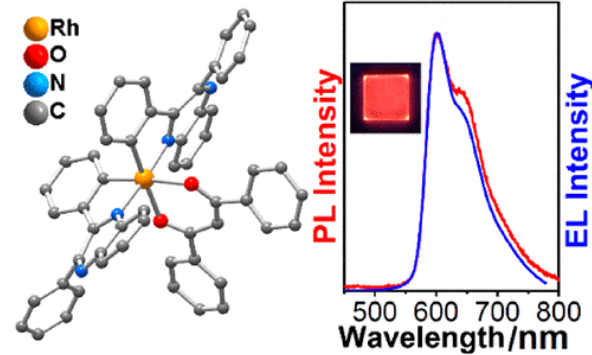
# Luminescence

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Excess energy can be dissipated through emission of light (*luminescence*): *photoluminescence* (PL, optical excitation) and *electroluminescence* (EL, electrical excitation).



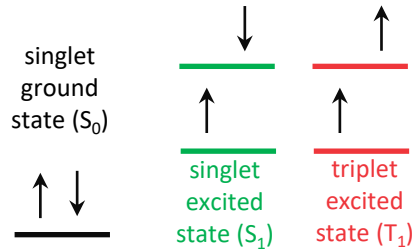
PL spectroscopy is a *contactless, non-destructive* method to probe material electronic structure



J. Am. Chem. Soc. 141, 32, 12863(2019)

PL and EL spectra of cyclometalated rhodium(III) complexes. *Aggregation and electron-exciton quenching* can induce differences between spectra.

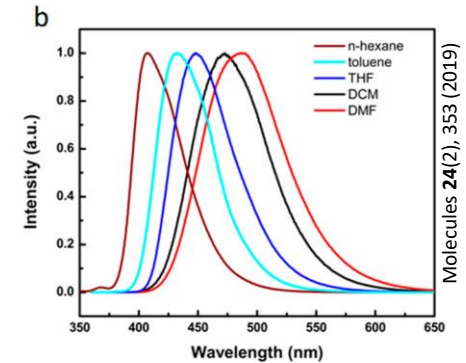
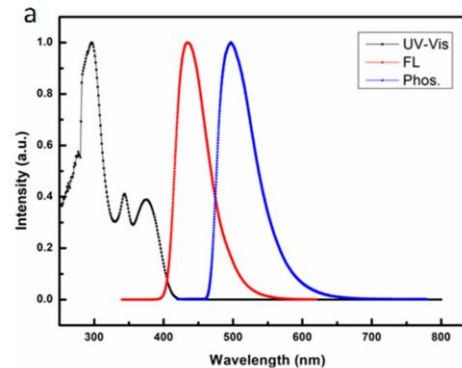
# PL: Fluorescence vs. Phosphorescence



**Fluorescence** and **phosphorescence** are both molecular photo-luminescence phenomena in which a molecule absorbs a photon and excites a species. **Fluorescence** (differently from phosphorescence) **does not change its electron spin state**, leading to *short-live electrons* ( $<10^{-5}$ s)

$$QY = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}}$$

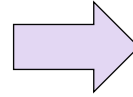
**Quantum Yield (QY),  $\Phi$  or Quantum Efficiency** measures the probability that a molecule will fluoresce or phosphoresce



(a) UV-VIS and fluorescence spectra of BCz-BFPz in toluene ( $10^{-5}$  mol/L) and phosphorescence spectrum of BCz-BFPz in 2-methylfuran solvent at 77K. (b) Fluorescence spectra of BCz-BFPz in different solvents ( $10^{-5}$  mol/L).

# (Bi)luminescent Materials

Transition from triplet ( $T_1$ ) to ground state ( $S_0$ ) is quantum *mechanically* forbidden  
 → triplets cannot spontaneously emit light

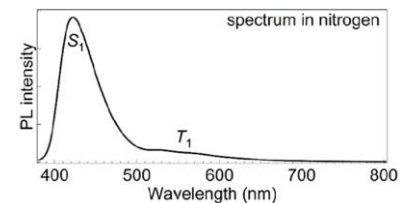
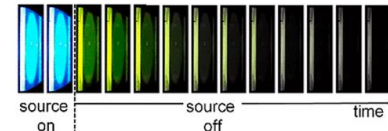
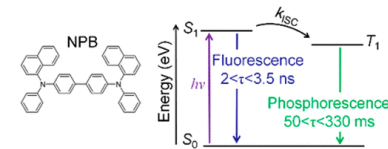


phosphorescence can be observed at very high efficiency if non-radiative channels are suppressed effectively

## bi-luminescent molecules

purely organic molecules can be designed in a way that allows thermal up-conversion from triplet to radiative fluorescent states (intersystem crossing, ISC)

**molecules with heavy transition metal atoms** (i.e. Ir), characterized by strong **spin-orbit coupling**, which unlocks radiative transition from  $T_1$  and additionally funnels singlets to these emissive triplet states, leading to phosphorescence



J. Phys. Chem. C **121**, 27, 14946 (2017)

# Summary

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## *Optical properties in organic semiconductors*

- *optical excitation of organic molecules* (depending on disorder)
- *exciton* and *luminescence*

## Next

*Characterization of organic materials* (in class, recording will be available)

