PHAS0058

Physics of Advanced Materials

Lecture 2: Organic Light Emitting Diodes

In this lecture…

OLEDs

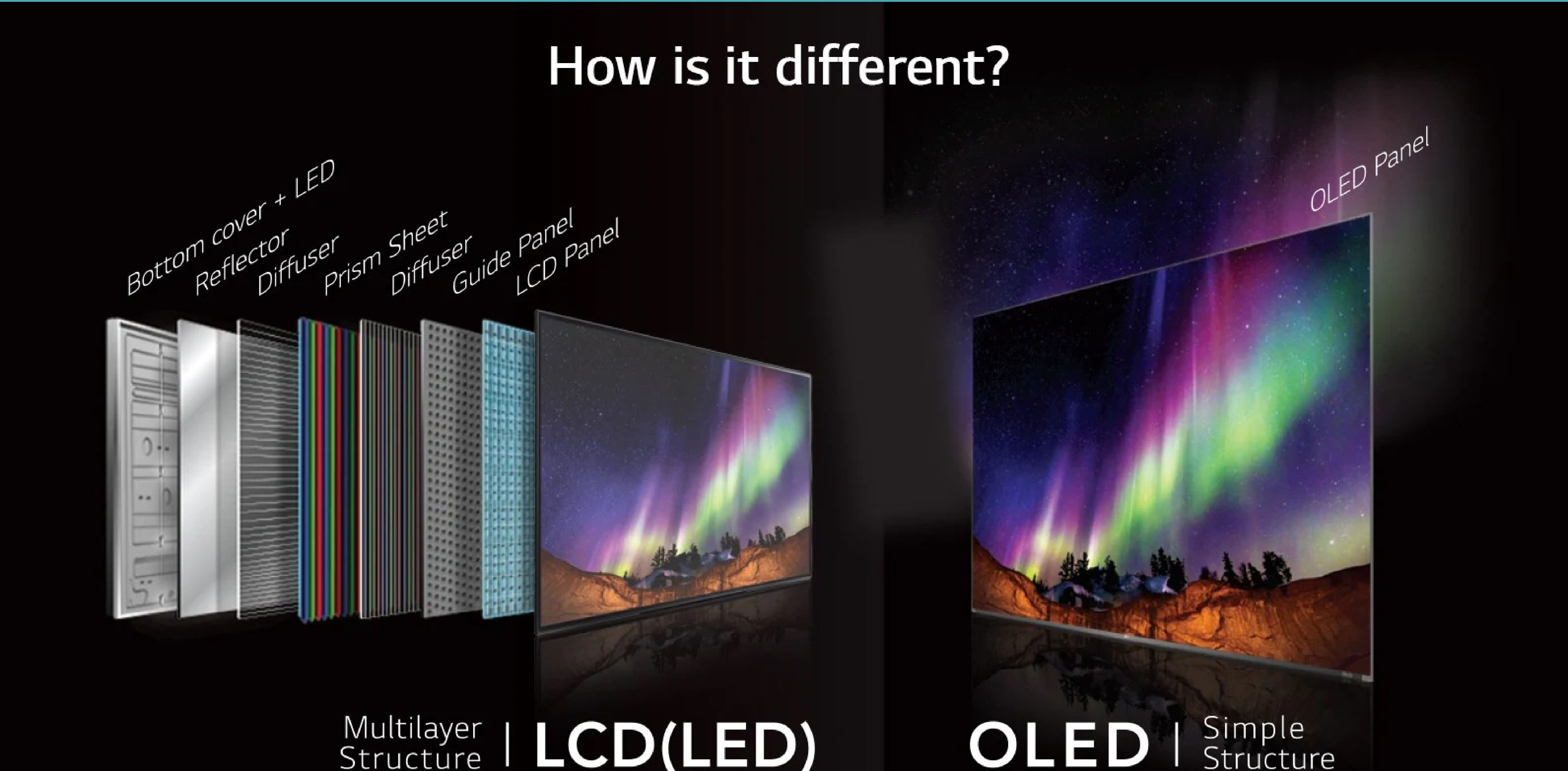
- overview of the field
- device structure and basic physics
- characterisation: parameters and efficiency
- optimisation: increasing EL

- luminance*

*self-study material

Overview of OLEDs

OLED displays



OLED displays

Advantages (compared to other materials):

- wide viewing angle
- flexibility
- low power consumption
- fast response time
- large spectral width (complete coverage)
- true-black
- self-luminous (no backlight)
- simple manufacturing (large area, flexibility, ultrathin, low cost)

Aim:

- high luminous efficiency
- colour purity
- device stability
- high yield at low cost

OLED vs. PLED

OLED

- LEDs made with small molecule materials
- already commercially available
- mix of 3 molecules for red, green and blue colors
- manufactured with vacuum eaporation

PLED

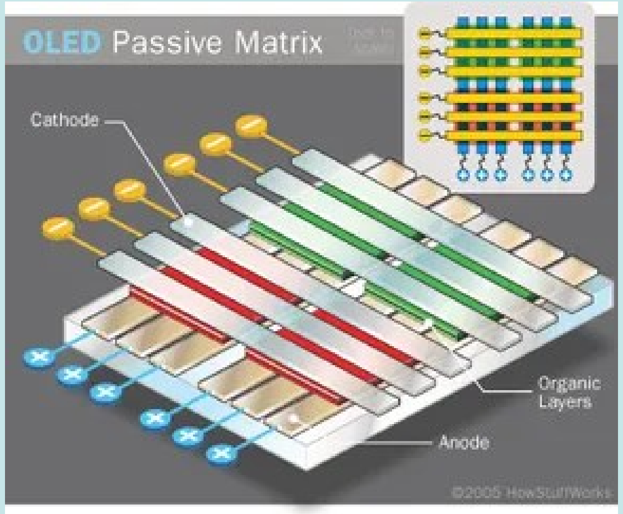
- LEDs made with polymers
- still in research phase (not yet competitive)
- use trichromatic materials
- manufactured using inkjet priniting
- potential for cheap large-scale flexible displays applications

*but mostly OLED refers to the whole class of ogranic LEDs, polymer and moleuclar ones

Passive vs. active matrix

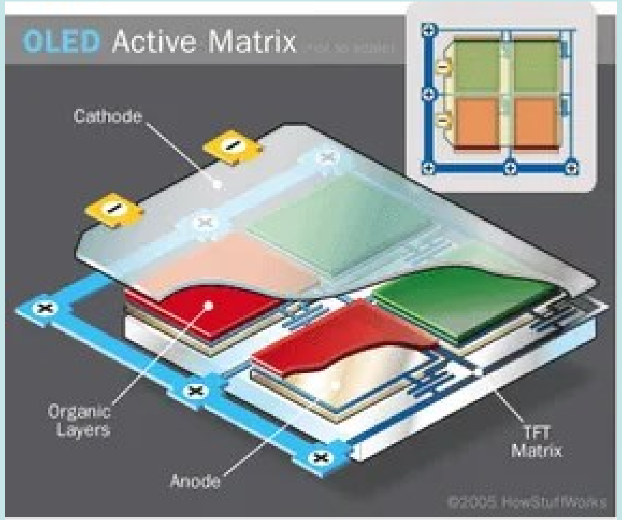
passive (PMOLED)

- cathode and anode make pixels
- easy to make
- high power consumption (compared to AMOLEDS)
- best for small screens



active (AMOLED)

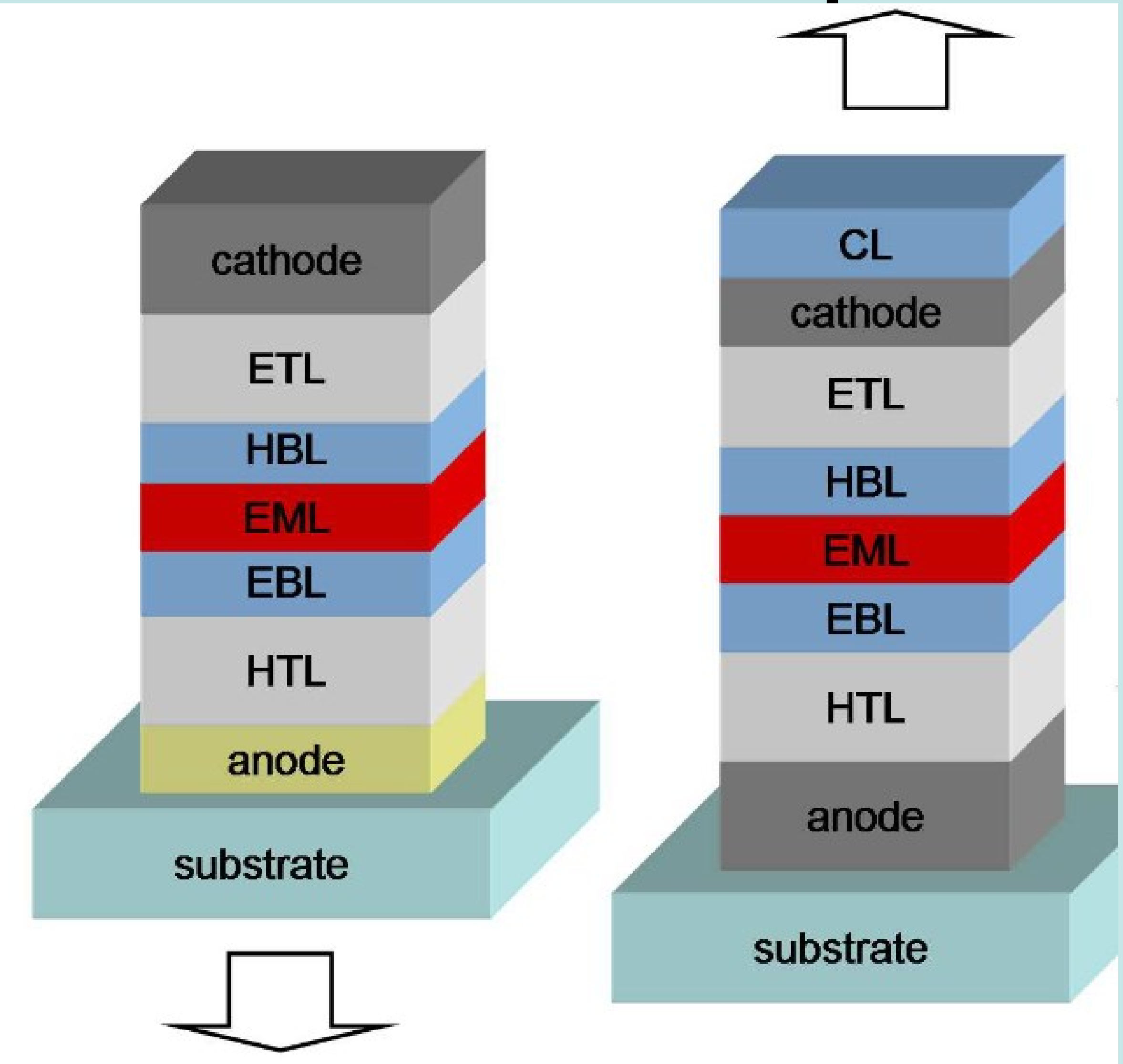
- additional layer of transistors (TFTs) matrix defining pixels
- low power consumption
- fast refresh rates
- great for large area applications



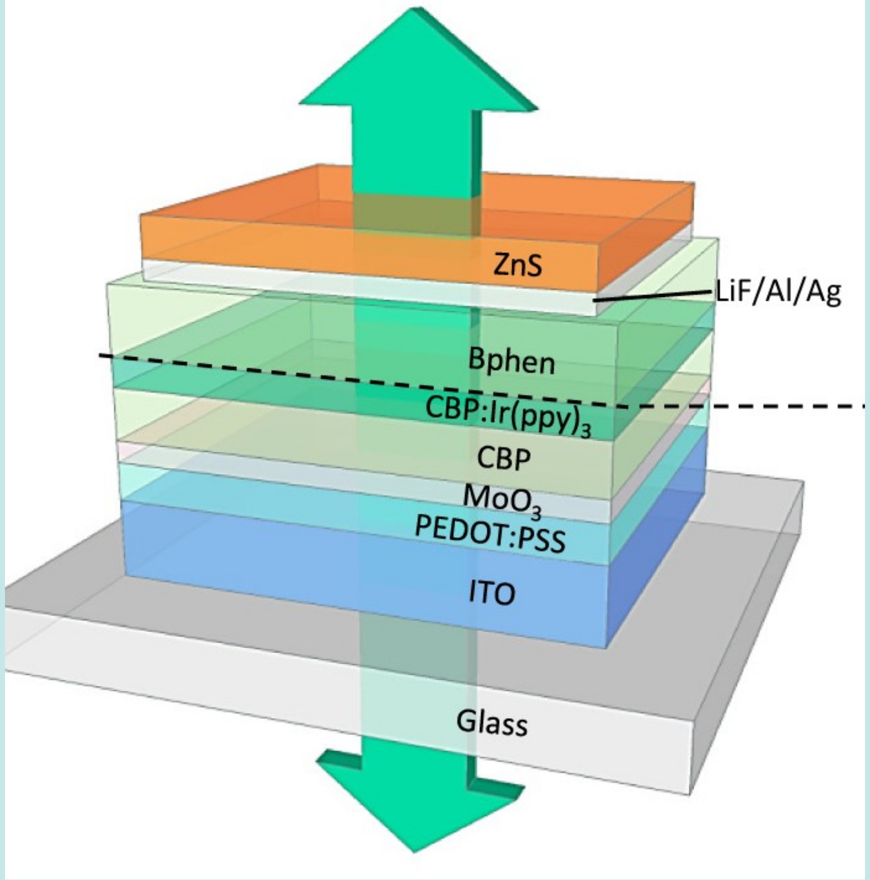
Images from HowStuffWorks.com

Main device structures

bottom emission **top emission**



transparent



H. Chung et al., Opt. Express **23**, 27306-27314 (2015)

Three generations of OLEDs

1st generation: fluorescent OLEDs

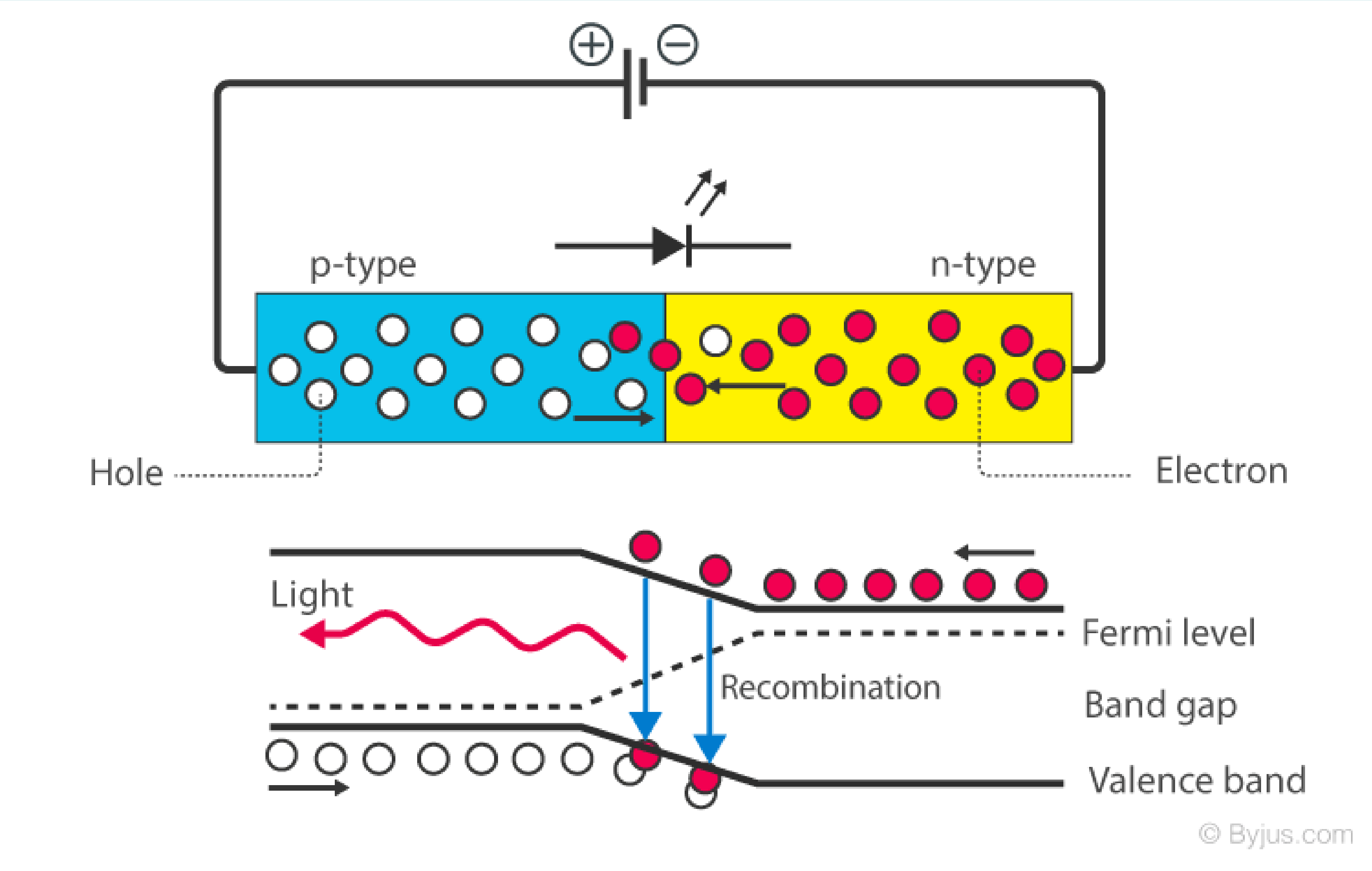
2nd generation: phosphorescent OLEDs

3rd generation: TADF OLEDs

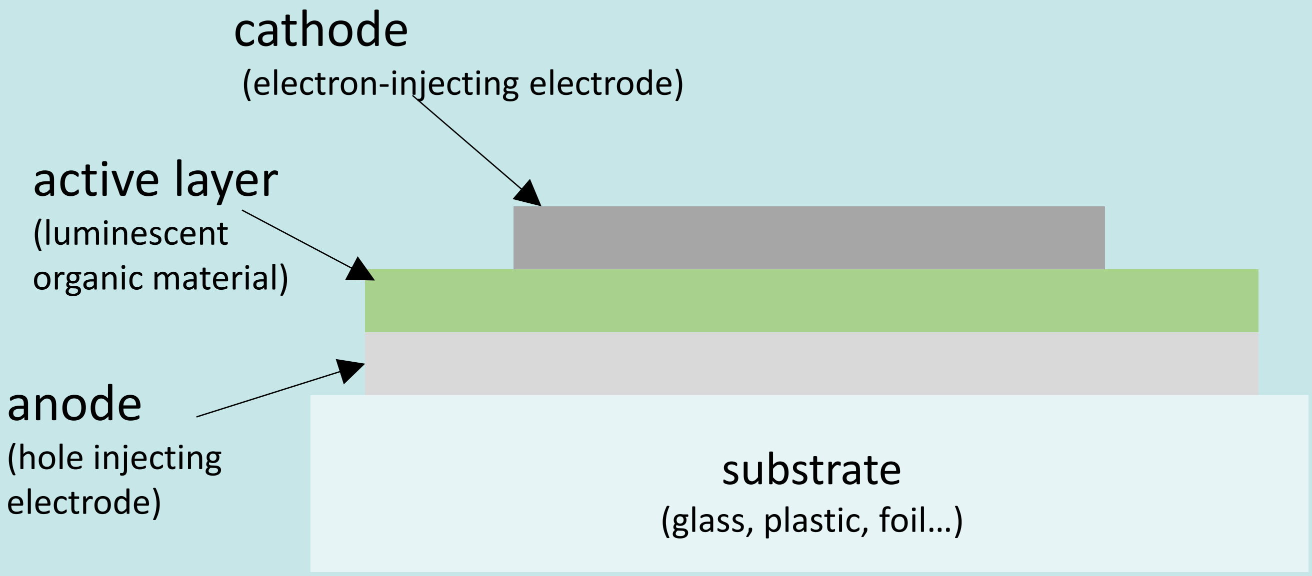
OLEDs – basic physics

What is an LED?

- Light Emitting Diode
- pn-juntion
- external bias
- ‘converts current into light’



What is in an OLED?



1965 monolayer model

Simplified operation

injection of charges

↓

charge transport

↓

exciton formation

↓

radiative recombination

Areas of research interest

injection of charges

charges trapped at the interface

charge transport

charges moving inefficiently, loosing energy

charges trapped at local defects

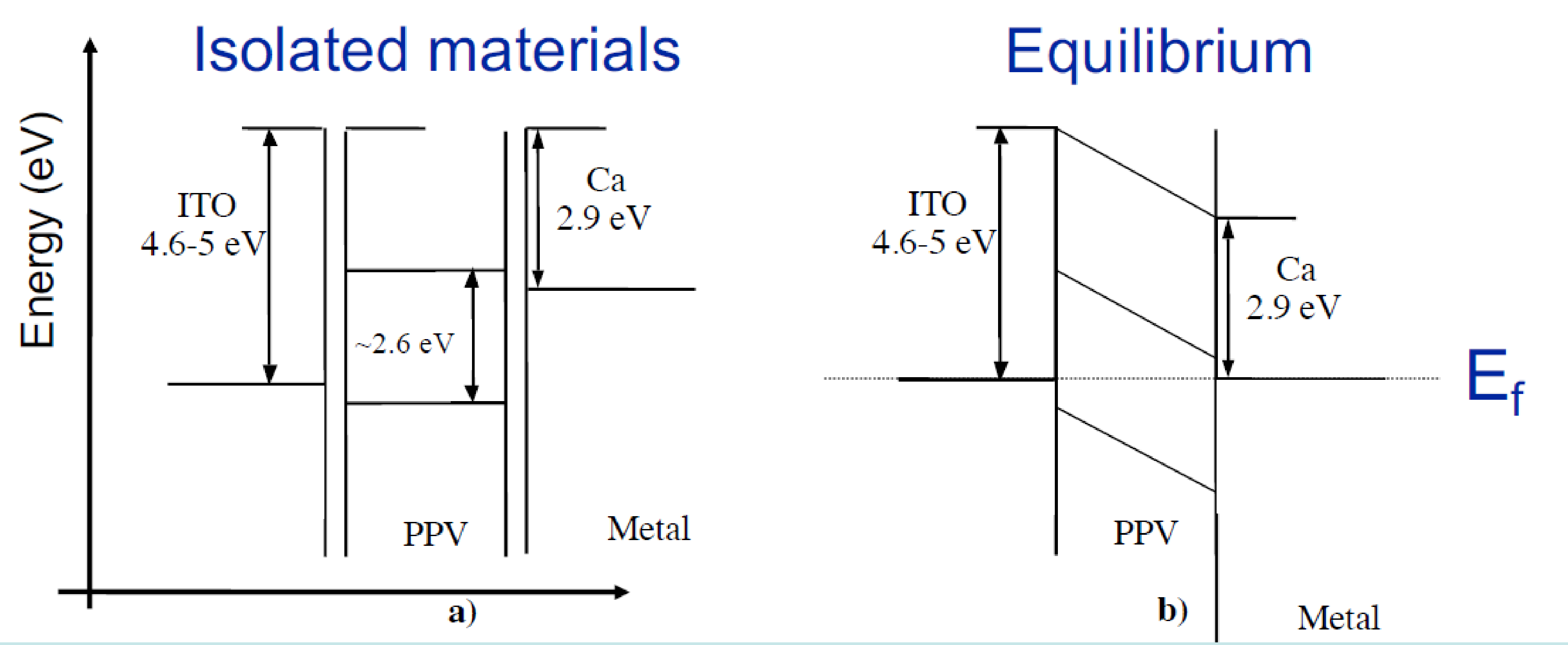
exciton formation

charges moving past the luminous material and into the opposite electrode

radiative recombination

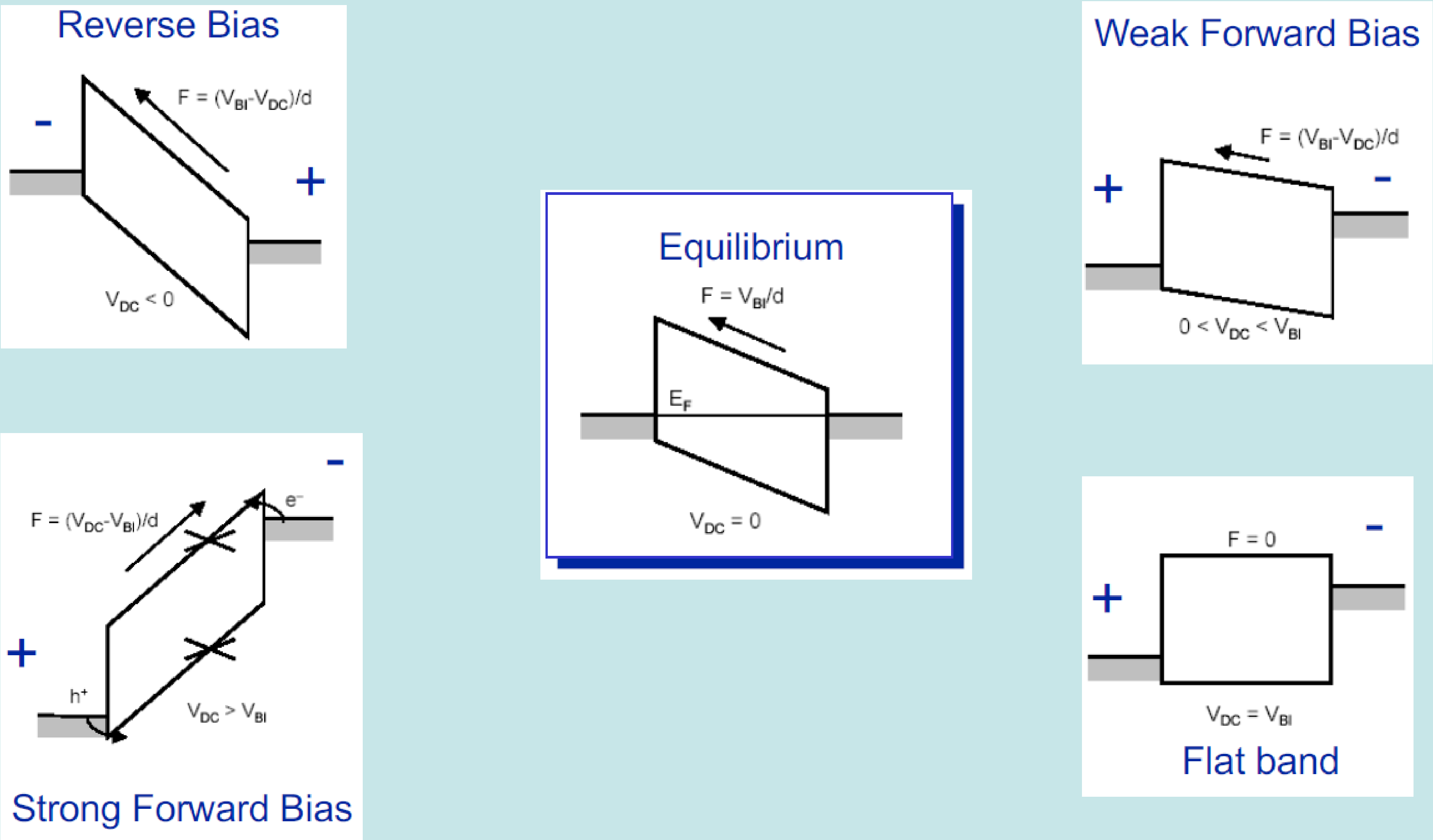
non-radiative recombination happens instead

Band diagrams of devices



- EF constant through the device at equilibrium
- charge transfer from cathode to anode
- built-in voltage VBI
- no charge accumulation on polymer
- bands rigidly tilted

Band diagrams for applied bias



Forward bias = low work function electrode -ve

OLED: stages of operation

voltage applied

e/h injected

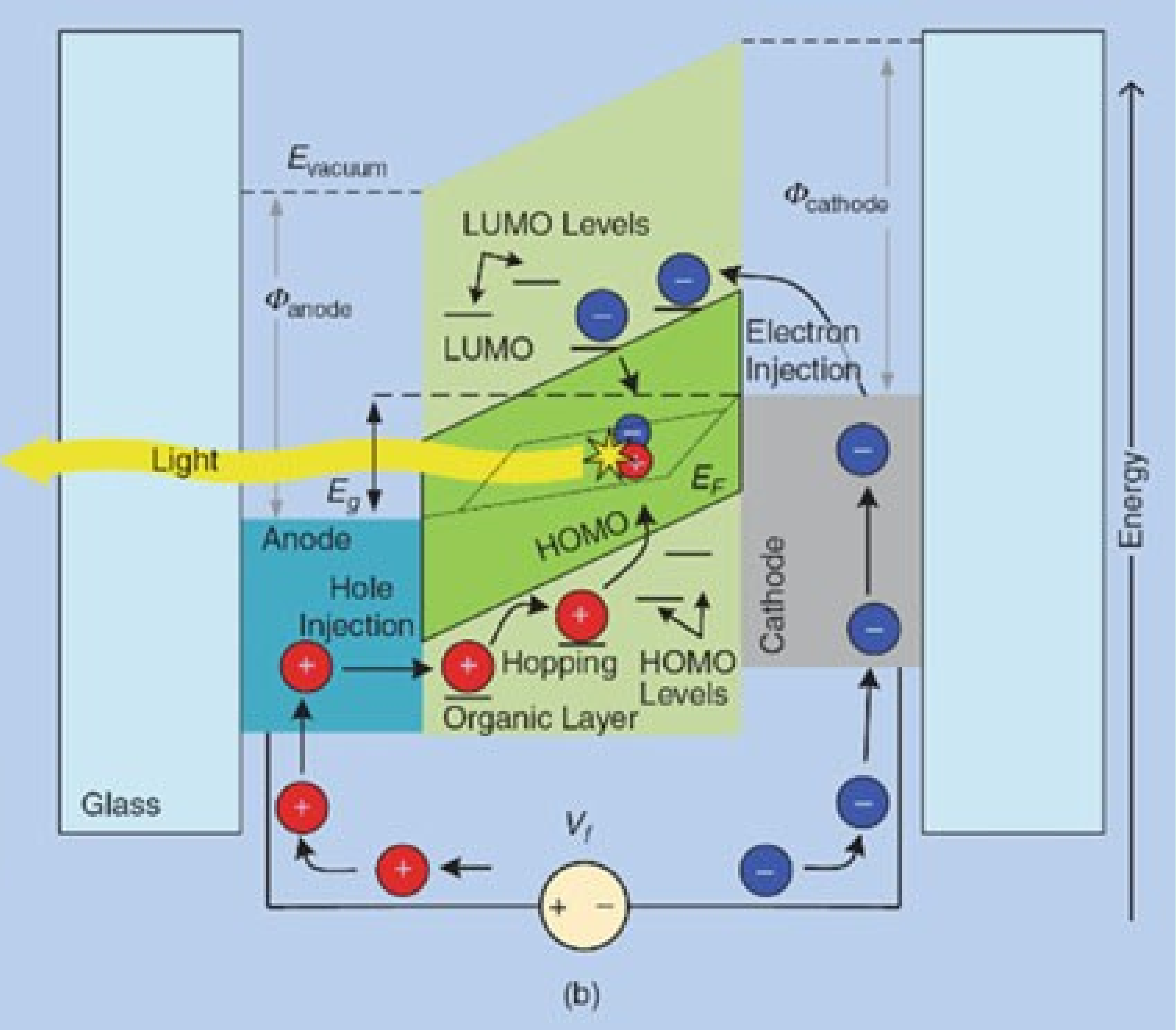
unstable exciton formed in host

energy transfer

to luminescent molecule (creation of excited state in dopant)

luminescence

(radiative recombination)



Characterisation of OLEDs

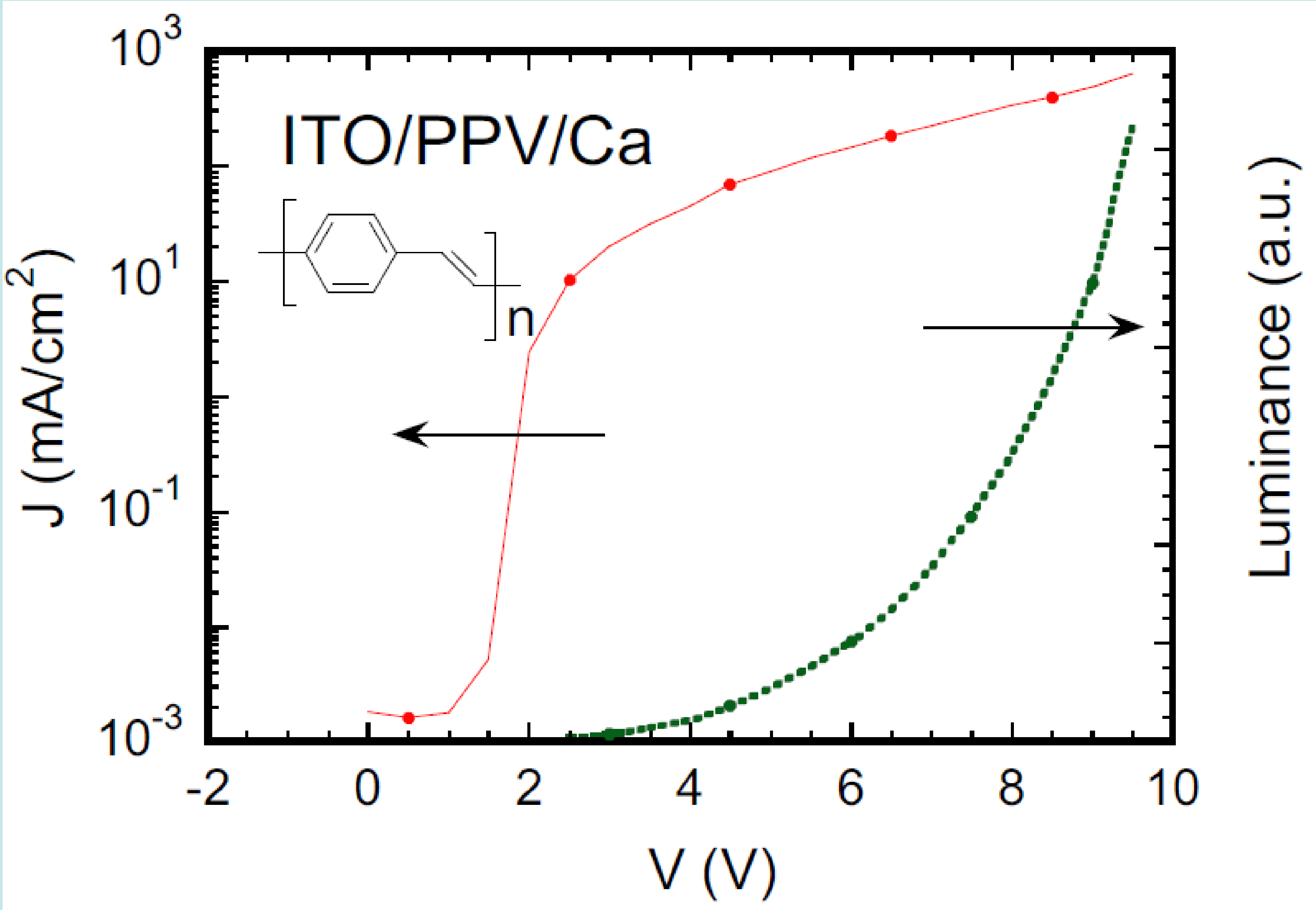
Desirable properties of an OLED

- low driving voltage (first EL experiments used 400V!)
- high luminance
- small driving current (high efficiency)

$$\eta_{lum} = \frac{\Phi_L}{V \cdot I} \left[\frac{lumen}{W}\right] \propto \frac{i}{V \cdot I} \left[\frac{cd}{VA}\right]$$

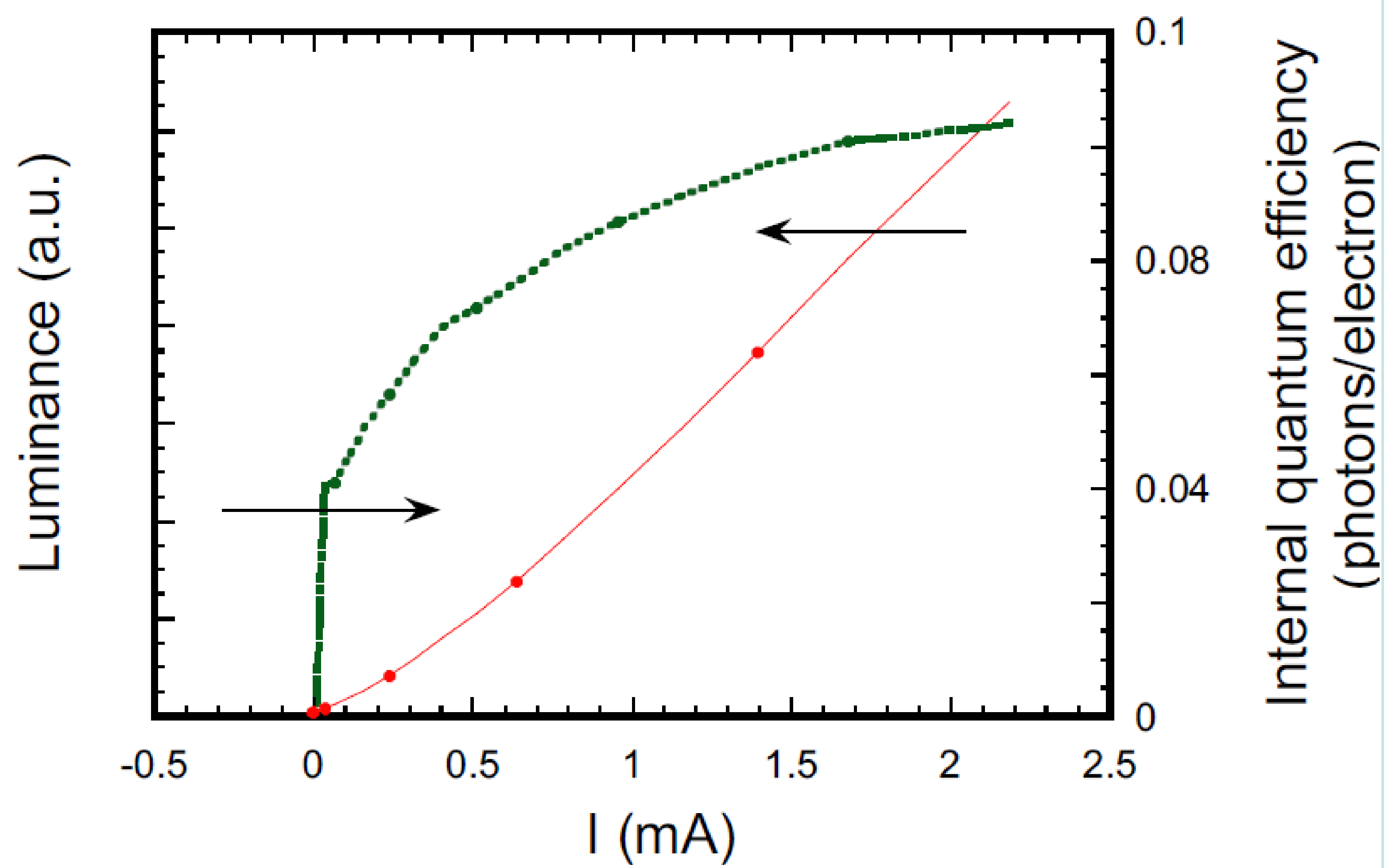
Φ_L - luminous flux [Lumen]
I – current [A]
i – intensity (luminance x area) [cd]

JV and LV characteristics



LJ characteristics

- injection barriers unequal to e and h
- low V = low current
- plateau as injection of minority carriers improves



Electroluminescence Quantum Efficiency

$$\eta_{EL} = \eta_{PL} \cdot r_{st} \cdot \gamma_{cap}$$

η_{PL} - photoluminescence efficiency → suppress non-radiative channels

r_{st} - ratio of singlet to TOTAL excitons → increase no. of radiative excitons

γ_{cap} - exciton formation factor → balance charge injection and transport

$$\gamma_{cap} = \frac{minority\ carriers}{majority\ carriers}$$

Optimisation of OLEDs

Overview of optimisation strategies

1. Increase $\boldsymbol{\eta_{PL}}$: suppress non-radiative decay channels
   a) prevent aggregation quenching
   b) optimise optical design to reduce quenching at electrodes
   c) reduce contaminations (chemical design of materials)

2. Increase $\boldsymbol{r_{st}}$: boost no. of radiative excitons
   a) increase the ratio of singlets to triplets
   b) use phosphorescence

3. Increase $\boldsymbol{\gamma_{cap}}$: improve e-h balance (exciton formation efficiency)
   a) balance charge injection
   b) balance charge transport

1a. Suppressing aggregation quenching

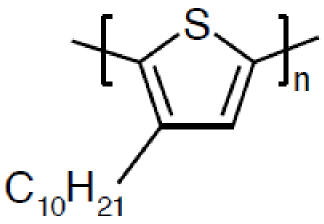
aggregation quenching – formation of dimers and cofacial aggregates leading to level splitting which prevents radiative decay

Solution: prevent close-packing of chromophores

- by diluting with matrix substance (leads to phase separation)
- by chemical design
  - change shape of molecules to reduce stacking
  - prevent phase separation

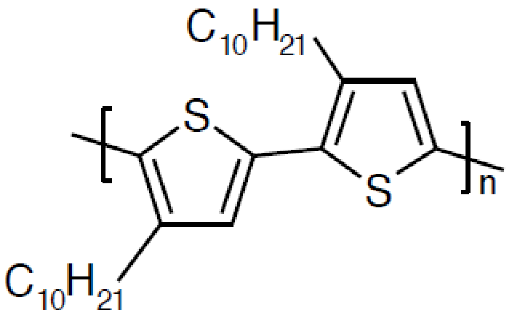
1a. Preventing stacking - polythiophenes

1)



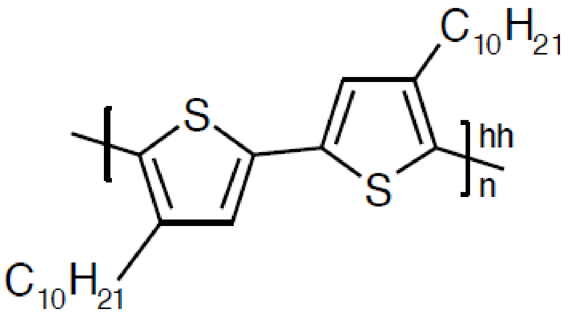
Non Regioregular
PL eff. ~2%

2)



Regioregular HT
PL eff. ~1%
High FET μ

3)

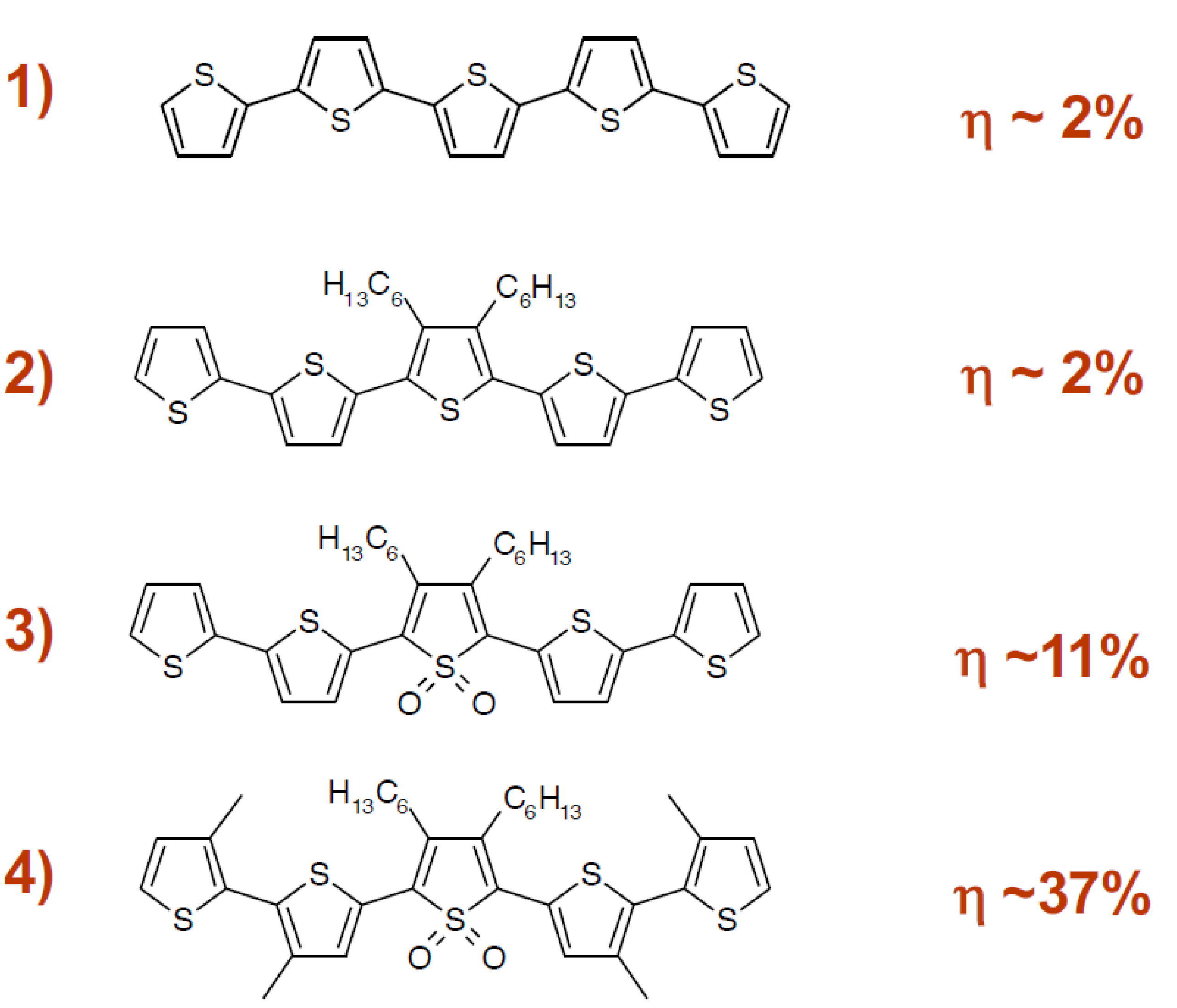


RR/HHTT
PL eff. ~11%

- large dihedral angles in HHTT configuration leads to lower crystallinity
- η_{PL} increases in HHTT

P. Barta, et al. J. Appl. Phys. 84, 6279-6284 (1998)

1a. Preventing stacking - oligothiophenes



- numbers are solid-state PL efficiency
- packing dominated by O-H interaction (rather than π-stacking

G. Gigli, R. Cingolani, G. Barbarella, L. Favaretto and F. Cacialli, Appl. Phys. Lett. 75, 439-441 (1999

1b. Optical device design

- multiple layers with various refractive indices:
- use intrinsic interference effects
- enhance interference with mirrors
- improve outcoupling
- reduce waveguiding
- create microcavities

J. Grüner, F. Cacialli and R.H. Friend, J. Appl. Phys. 80, 207 (1996).
G.R. Hayes, F. Cacialli and R.T. Phillips, Phys. Rev. B 56, 4798 (1997).
S.E. Burns, et al. Optic. Mater. 9, 18 (1998).

Overview of optimisation strategies

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2. Increase r_{st}: boost no. of radiative excitons
    a) increase the ratio of singlets to triplets
    b) use phosphorescence

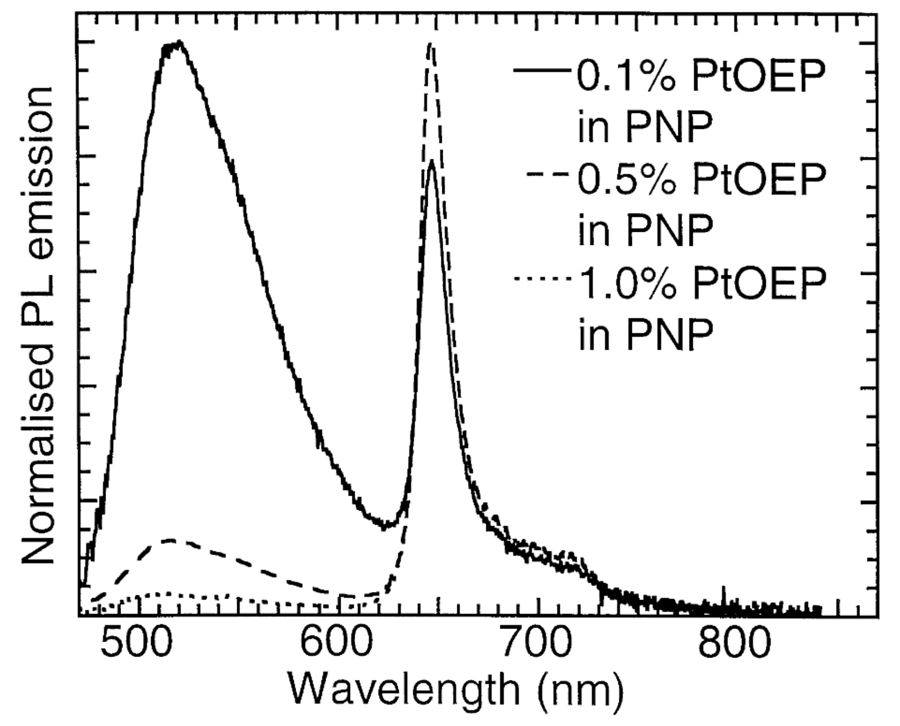
3. Increase γ_{cap}: improve e-h balance (exciton formation efficiency)
    a) balance charge injection
    b) balance charge transport

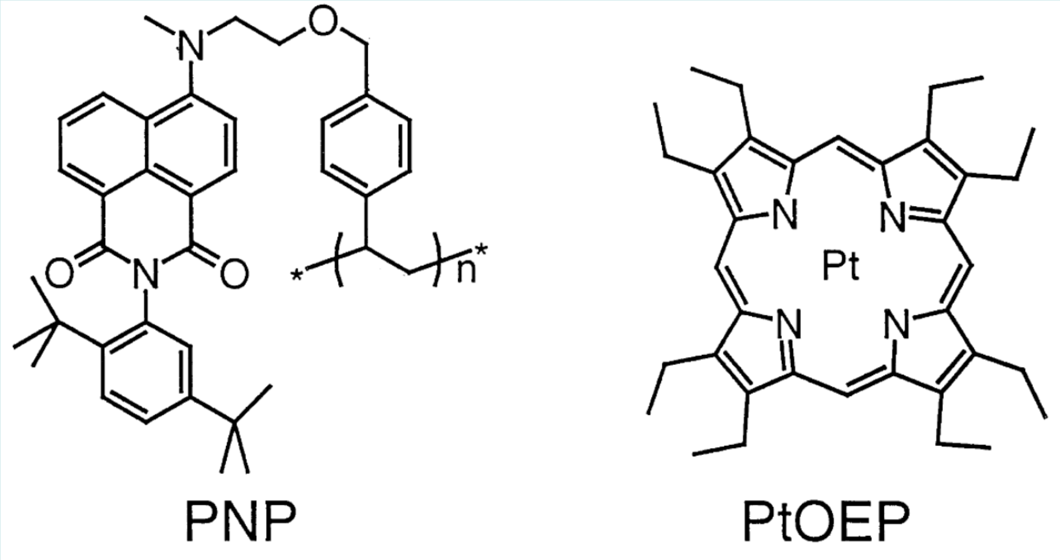
2a. Improving no. of radiative excitons

- TTA (Triplet-Triplet Annihilation)
  - fusion of two triplets into a singlet (and other species): $T_1 + T_1 \rightarrow S_n + S_0$
  - mainly in anthracene derivatives
  - usually requires higher driving voltage
  - max theoretical PLQY: 62.5%, in practice <40%
- TADF (Thermally Activated Delayed Fluorescence)
  - aka reverse ISC: triplet promoted to singlet
  - possible when kT comparable to Exchange Energy
  - max theoretical PLQE: 100%
- HLCT (Hybrid Local Charge Transfer)
  - requires donor-acceptor molecule with similar triplet and singlet energies
  - creates coupled charge-transfer state (easy conversion) and local excited state (efficient and fast fluorescence)
  - max theoretical PLQY: 100%

2b. Harvesting phosphorescence

- theoretical max PLQY 100% if assisted by ISC
- use small molecular weight fluorescent host to decrease concentration quenching
- 3 possible paths (Cleave at al.):
  - Foerster transfer of singlets from host + ISC
  - Dexter transfer of triplets from host
  - e-h capture directly in the guest emitter





V. Cleave, et al. Adv. Mater. 11, 285 (1999)

Issues:
- usually high TTA in phosphorescent materials
- difficult to find blue emitters
- efficiency drop at large currents (saturation of emissive sites due to long lifetime)
- Dexter transfer slow because of range

Dr Monika Szumilo

2b. Transfer requirements

Foerster transfer:

- energy of host molecule > guest
- spins of host and guest remain unchanged before and after transfer
- emission spectrum of host overlaps with absorption spectrum of guest (transition coupling)

Dexter transfer:

- energy of host molecule > guest
- total spin of electrons conserved
- emission spectrum of host overlaps with absorption spectrum of guest (transition coupling)
- orbital wave functions of host and guest overlap

Overview of optimisation strategies

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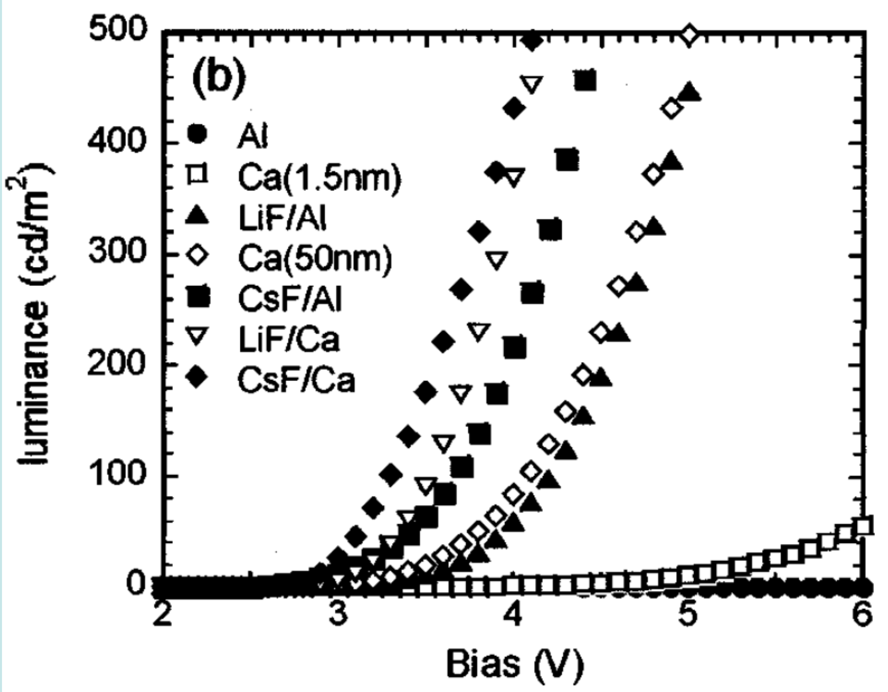
   a) balance charge injection
   b) balance charge transport

3a. Balancing charge injection

Cathode (e injection):

- reduce work function by adding Ca, Li, LiF or Al
- especially important in blue-emitting materials (large bandgap)



Brown et al JAP, 93, 6159 (2003)

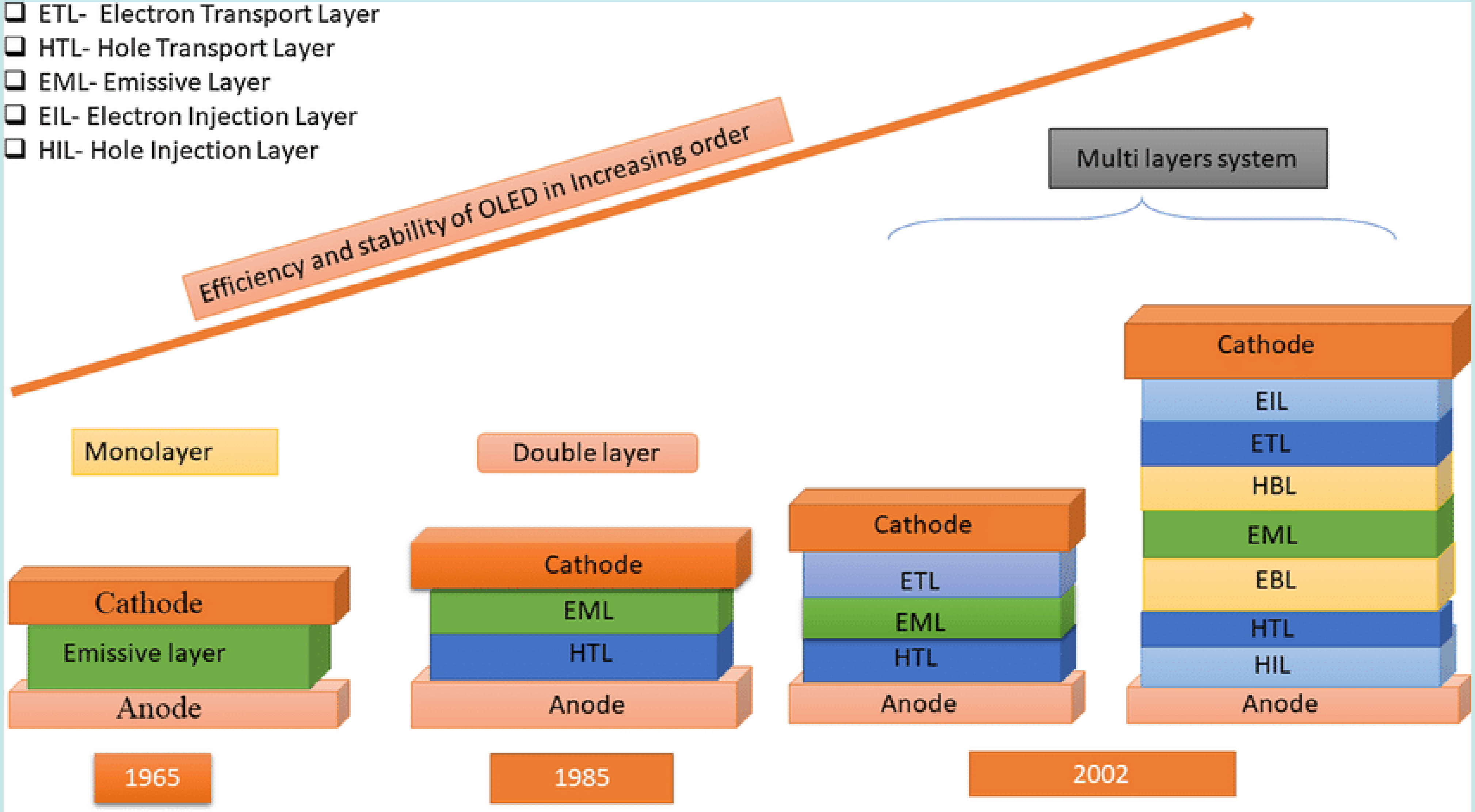
Anode (h injection):

- reduce work function of ITO by:
  - self-assembled monolayers
    PKH Ho et al. Adv. Mater. 10, 769 (1998)
    de Boer et al. Adv. Mater. 17, 621 (2005)
  - spin-coated layers
    SA Carter et al. Appl. Phys. Lett. 70, 2067 (1997)
    TM Brown et al Appl. Phys. Lett. 75, 1679 (1999)
  - layer-by-layer deposition of progressively de-doped layers
    P Ho et al Nature (2000)
  - oxygen plasma treatment (standard)
    JS Kim, et al. J. Appl. Phys. 84, 6859 (1998)

3b. Balancing charge transport

- **reduce excess majority carriers (generally holes)**
- **introduce separate electron and hole transporting layers**
  - holes: aromatic triamines, carbazole compounds, organosilicons, organometals, etc.
  - electrons: planar aromatic compounds wth large conjugate structures, metal complexes (e.g. Alq_3), oxadiazoles, perfluorinated materials, thiophene oligopolymers
- **formation of heterojunctions**
  - increased efficiency and improved characteristics thanks to recombination at polymer-polymer junctions
  - possibility to control the position of recombination region (reduce electrode quenching)
  - increased driving voltage (additional barrier in the device) and reduction of operative lifetime
  - complex fabrication procedure

Progression of device structure



Bauri J, Choudhary RB, Mandal G (2021) Recent advances in efficient emissive materials-based OLED applications: a review. J Mater Sci 56:18837–18866

Summary

- still some problems after 70 years of development
- current trends:
  - find blue phosphorescent materials with good efficiency and stability
  - TADF and HLCT to improve exciton use in fluorescent materials
  - better performance for inkjet printed devices (compared to vacuum deposition)
  - improved power efficiency overall (charge injection, exciton utilisation and outcoupling of light)

Next:

Organic Photovoltaics (OPVs)