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Organic light emitting diodes and rare-earth complexes

Herbert Boerner SSL
PFLA

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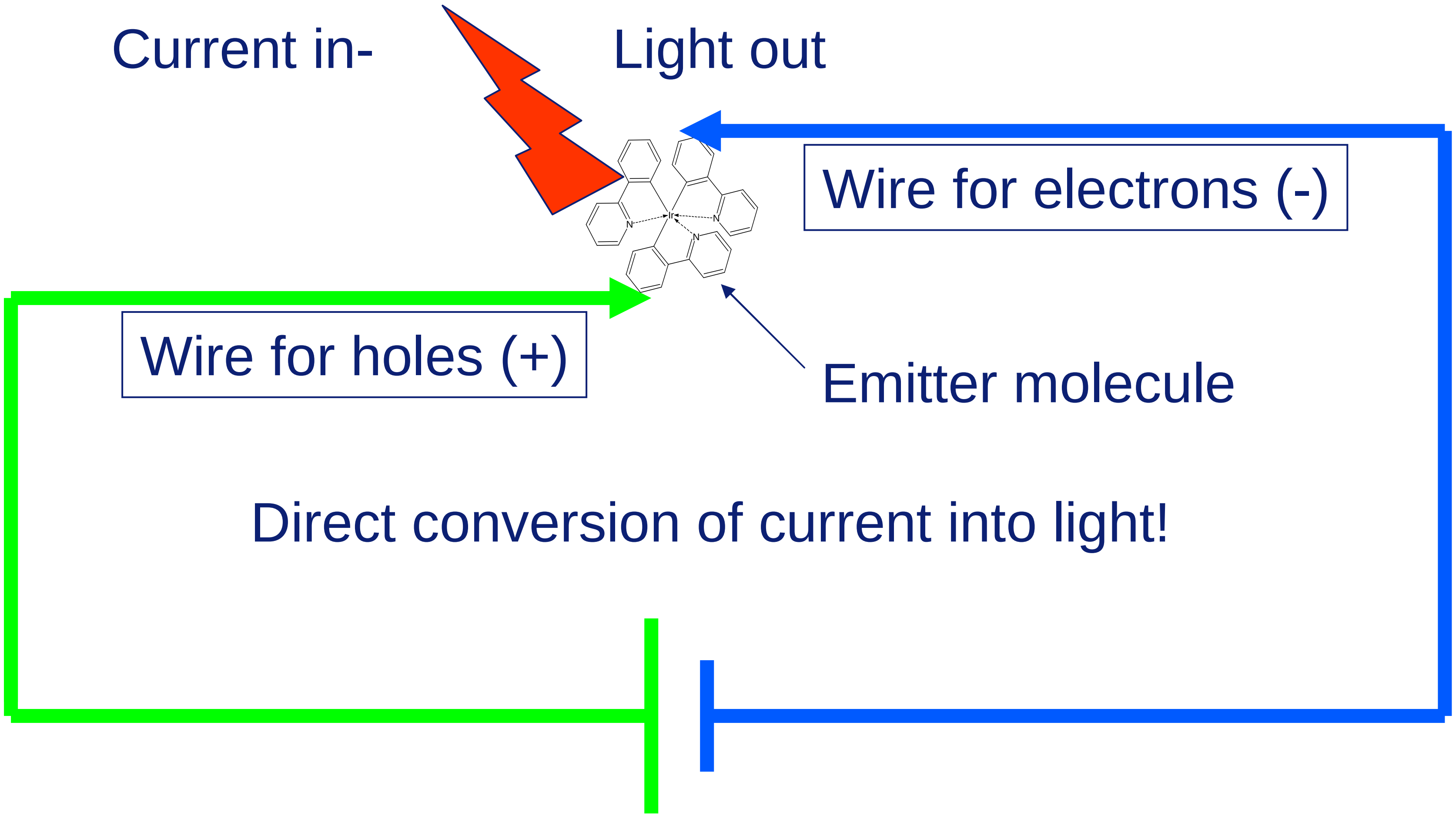
The magic of light

OLEDs is all about electro-excitation of organic molecules- what we are trying to achieve?



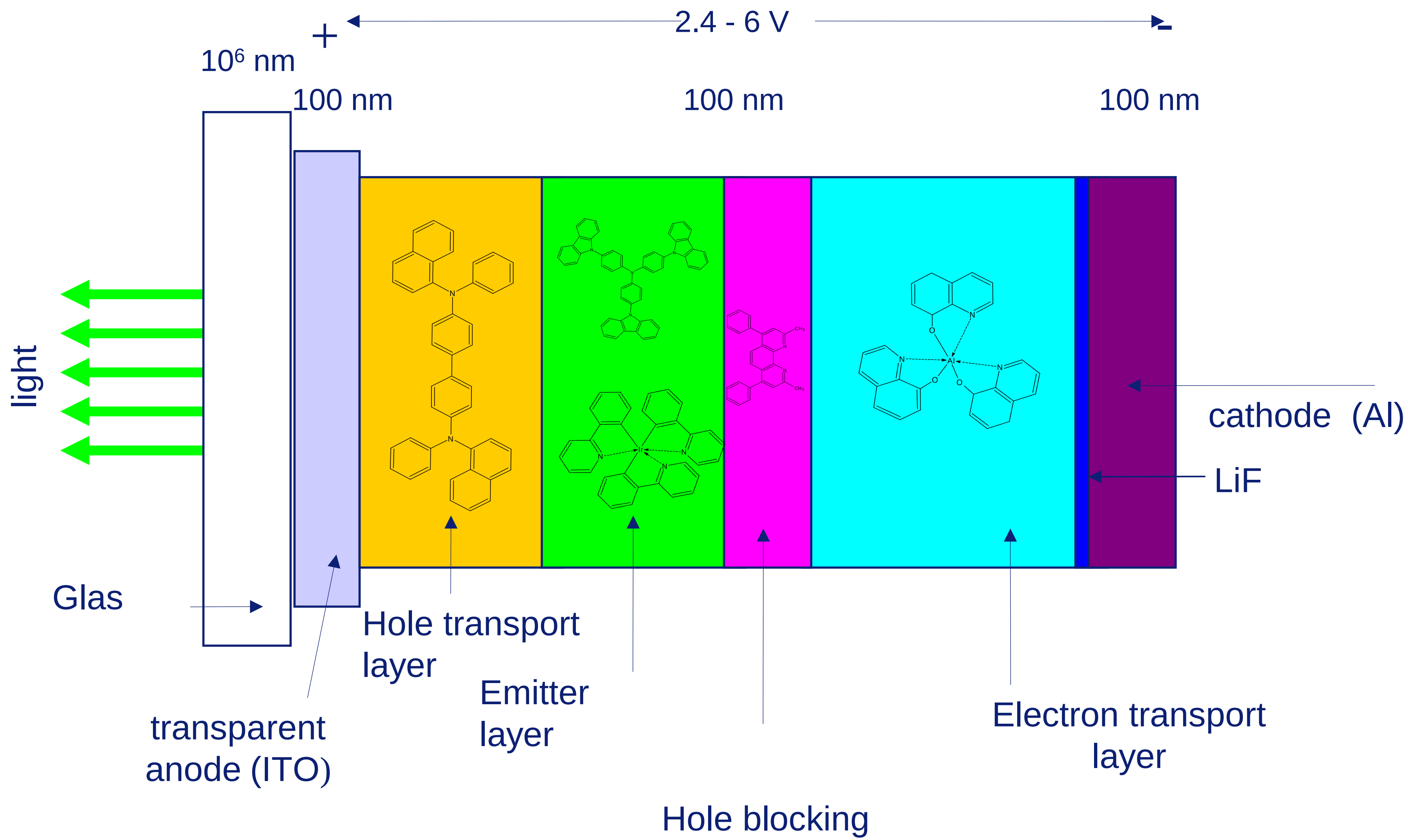
Outline of tutorial

- **OLED fundamentals**
  - charge injection
  - charge transport
  - recombination
  - light emission
- **Organic emitters in OLEDS**
  - fluorescent emitters
  - phosphorescent emitters
- **(Artificial) lighting fundamentals**
  - Relevant quantities and units
  - Conventional light sources
  - Color mixing and color quality
  - OLED design options
- **Rare-earth emitters for OLEDs**
  - function of ligands
  - matrix requirements
  - saturation problems
  - limitations
- **OLEDs for lighting**
  - application areas and requirements

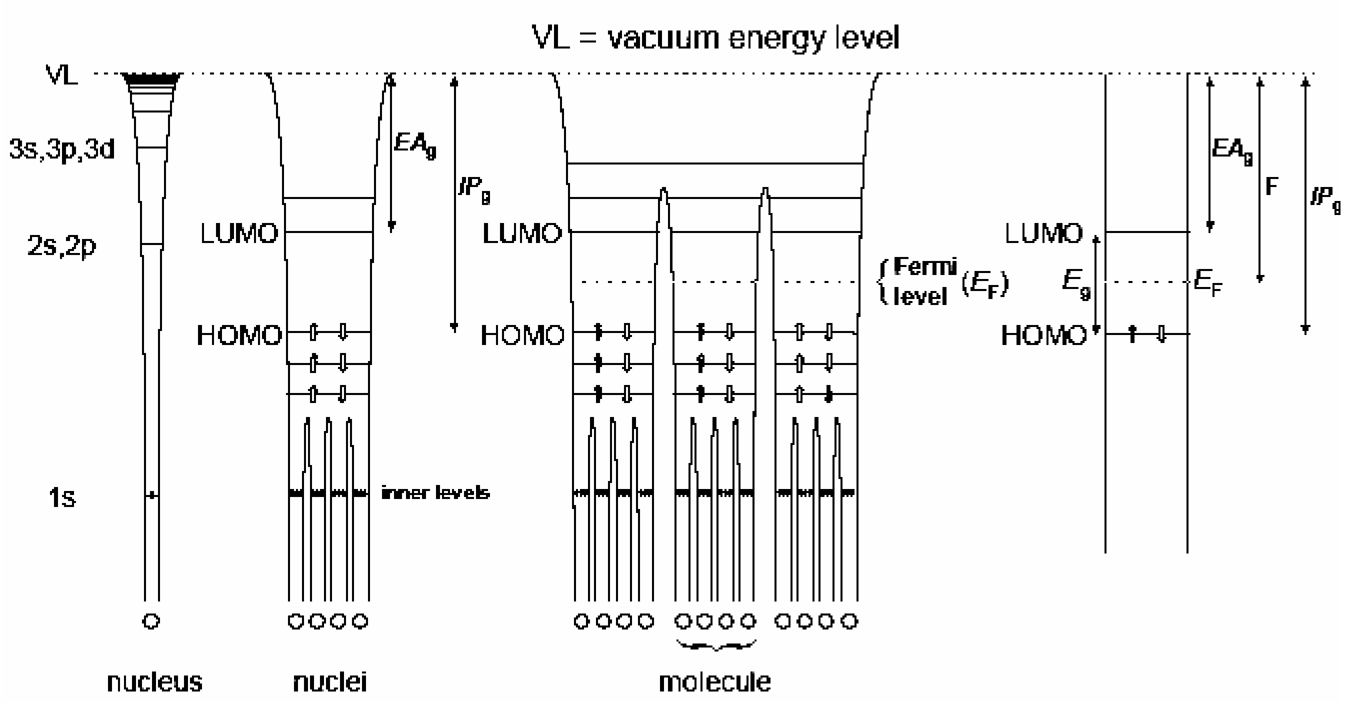
PHILIPS A bit of organic electroluminescence history…

- 1965: Helfrich and Schneider : First EL experiments with anthracene single crystals
- Around 1973: PVK as hole conductor
- 1980-85: introduction of organic charge conductors in copying machines and laser printers
- 1987: Tang, van Slyke at Kodak: first “modern” two-layer OLED with green emitter ALQ3
- 1990: first Polymer LED: Burroughs, Friend
- 1991: First proposal to use RE-emitters: Kido
- 1994/95: first own tests on Eu-complexes
- 1999: M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, and S. R. Forrest: first OLED with Iridium complex as triplet emitter

Typical OLED design



Representation of the electronic structure in an organic solid



H-atom | molecule | molecular solid | schematic representation

OLED fundamentals

Amorphous solid versus crystalline solid

Two different models:

Semiconductor band model,

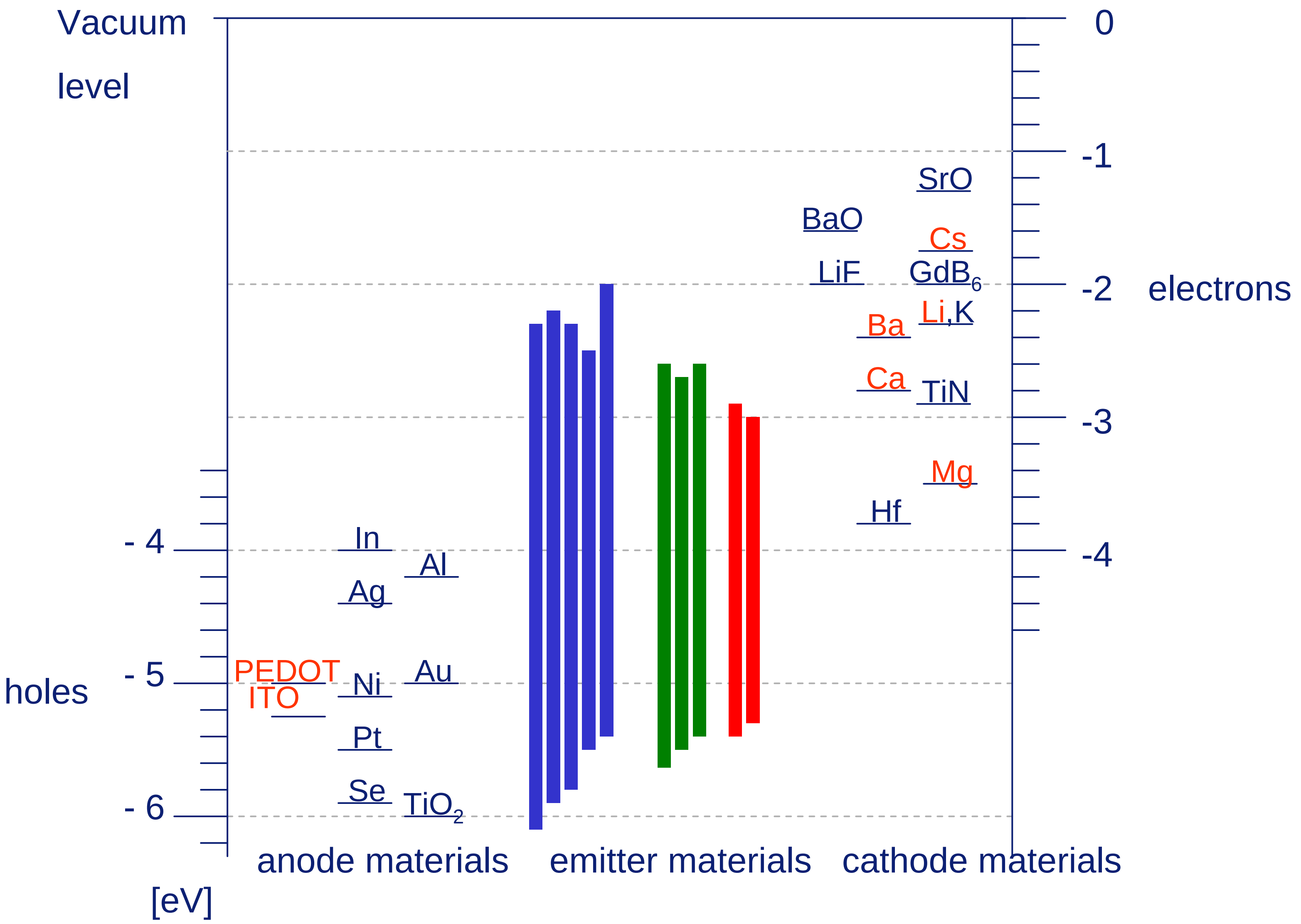
- crystal,
- regular lattice,
- delocalized states (over many molecules),
- strong interaction between molecules,

Organic glass:

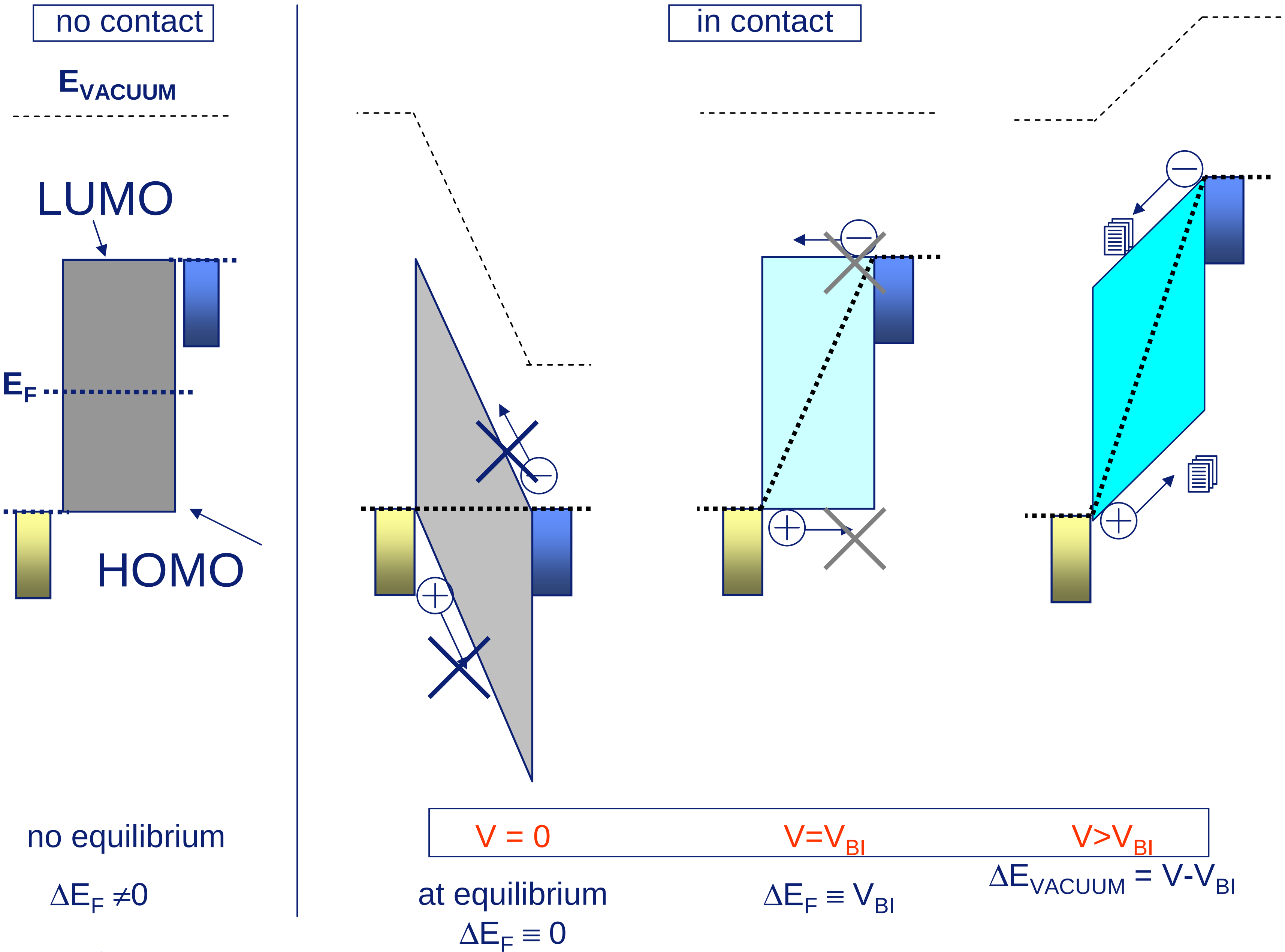
- frozen liquid,
- irregular packing,
- localised states (on one molecule),
- weak interaction between molecules

Organic glass needed for electrical isolation: no breakdown at h electric fields

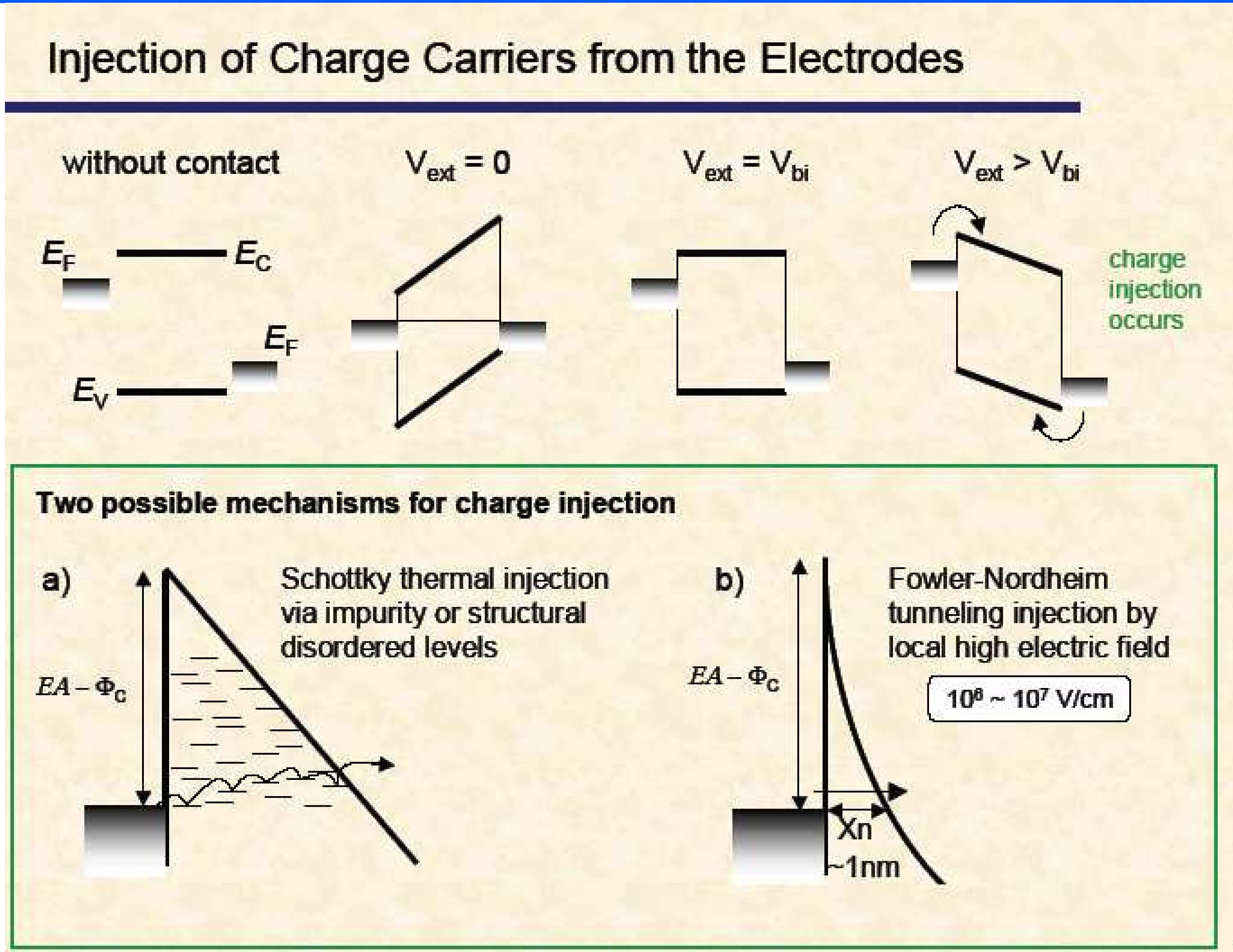
OLED fundamentals: charge injection



OLED fundamentals: band model

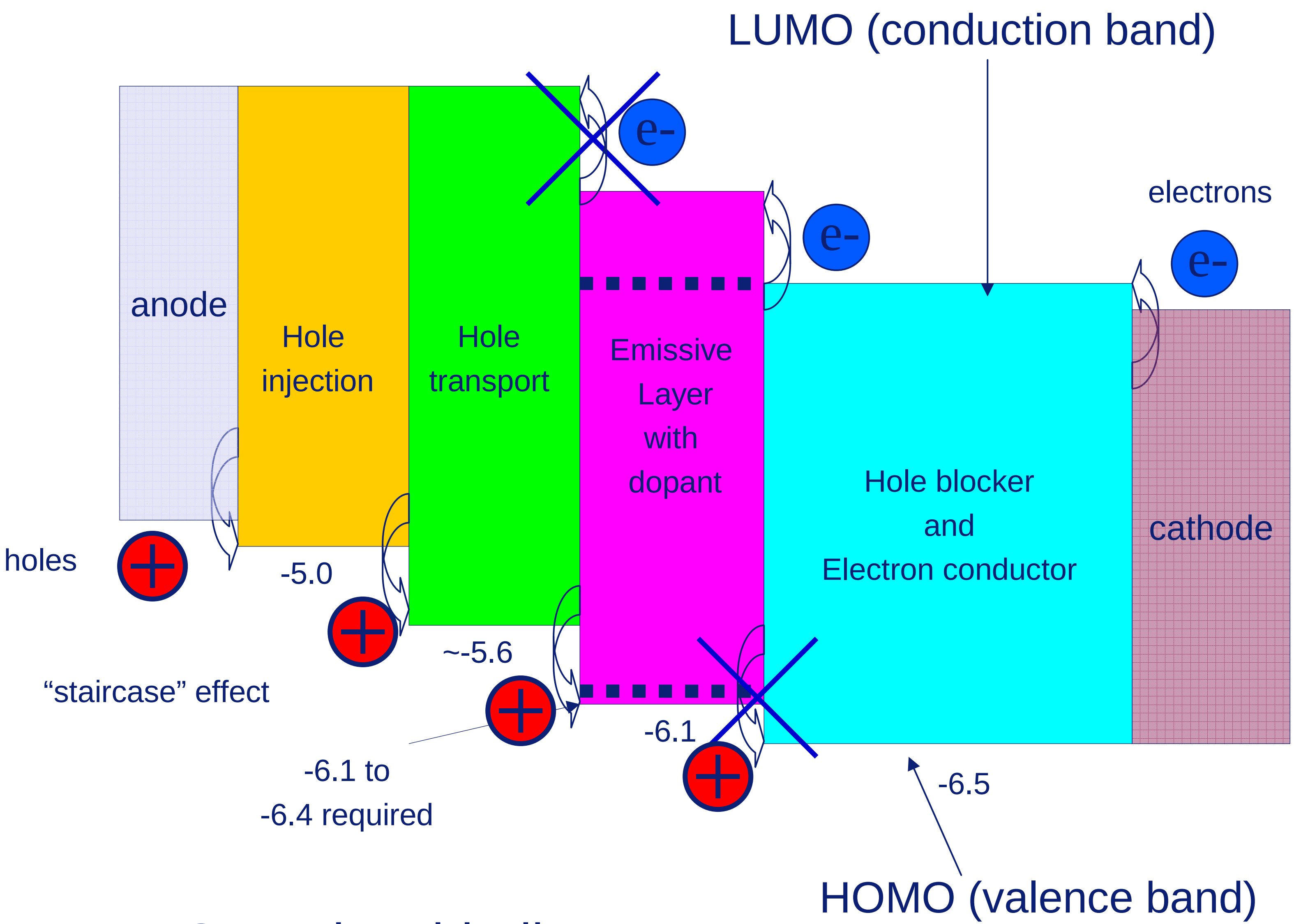


OLED fundamentals: band model



HOMO-LUMO levels: relation to
redox potentials => Fc+/Fc: -4.8 eV

OLED fundamentals: energy barriers



LUMO: exciton binding energy!!

OLED fundamentals: charge transport …

- Organic materials are basically high-bandgap isolators when undoped
- High electric fields required to transport charge:
  - 10V / 100 nm => 100 kV/mm !!!!
- Drift velocity v: $v = \mu E$ where μ mobility
- Drift is thermally activated
- Mobility in glassy organics: $10^{-3} – 10^{-7}$ $cm^2/Vsec$
- Mobility in organic crystals: $10^{-2} – 10^{1}$ $cm^2/Vsec$

PHILIPS OLED fundamentals: charge transport

Transport of Charge Carriers in Organic Solids

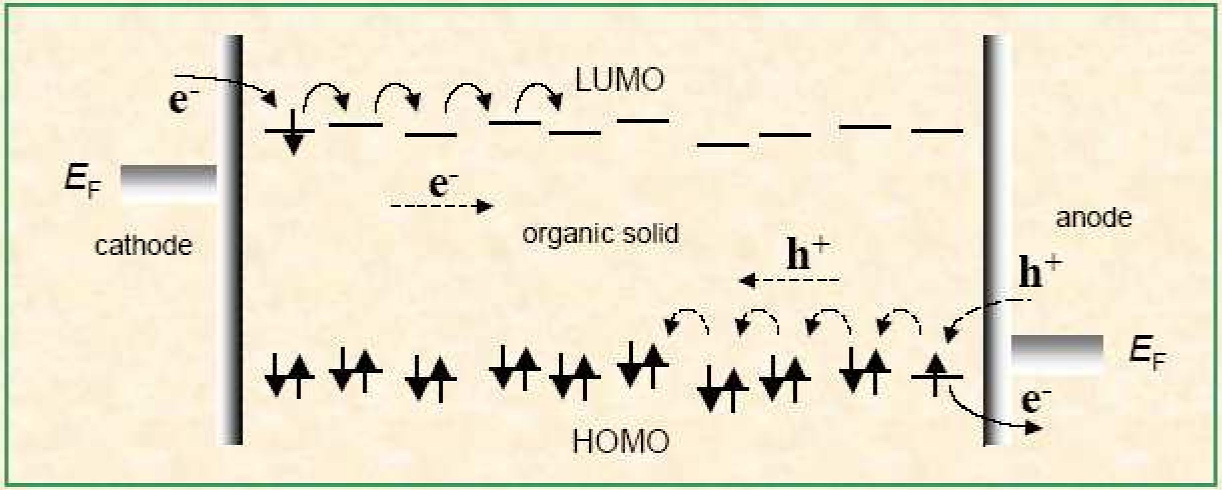
Bässler: thermally activated hopping process on Gaussian distributed energy niveaus

$$\mu = \mu_0 \exp\left[-\left(\frac{2\sigma}{3kT}\right)^2\right]\exp\left[C\left(\frac{\sigma^2}{(kT)^2}-\Sigma^2\right)E^{1/2}\right]$$

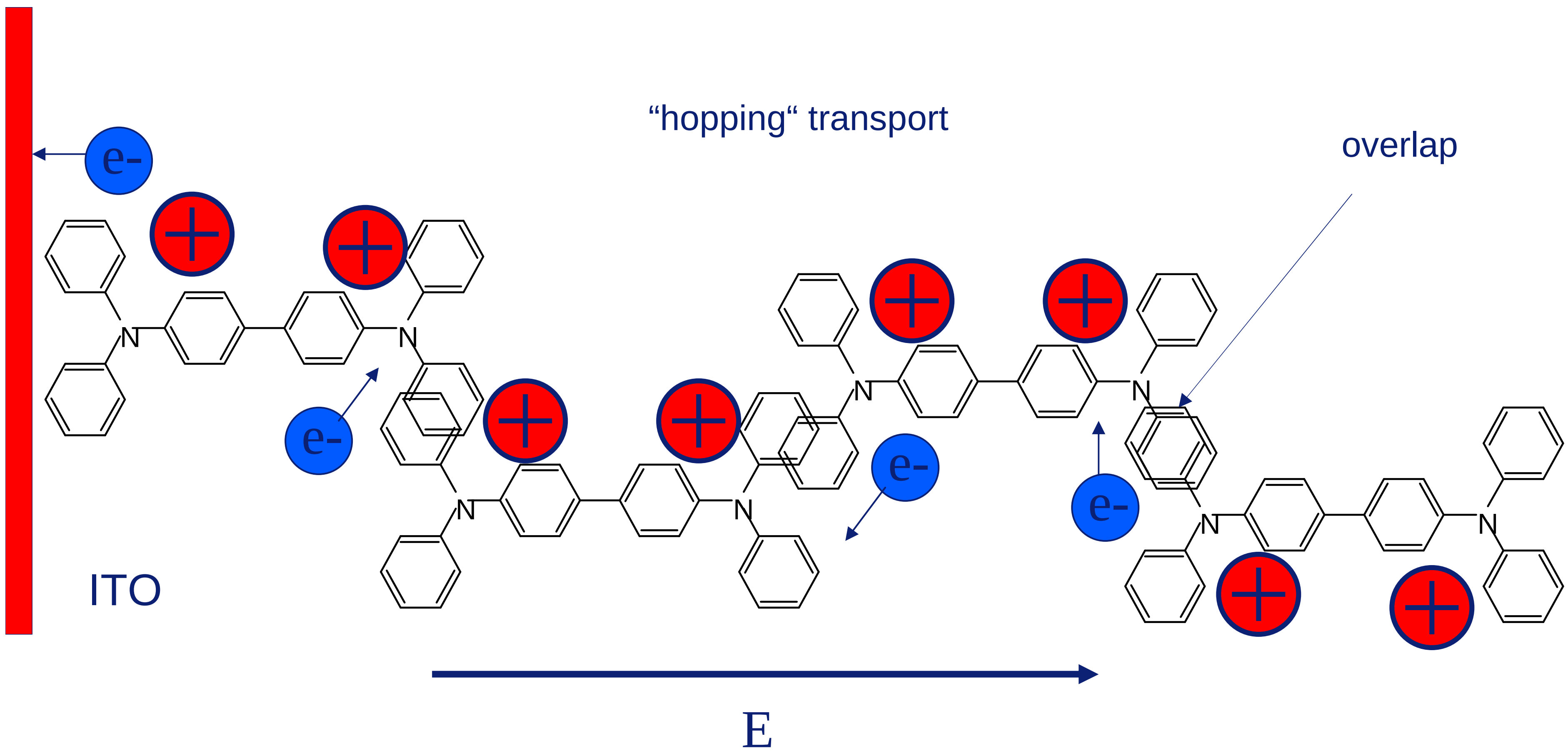
temperature and field dependend carrier mobility

(C = empirical konstant $2{,}9 \cdot 10^{-4}$ $cm^{1/2}\,V^{-1/2}$)

σ = energetic (diagonal) variation, Σ = positional (off-diagonal) variation of the hopping sites



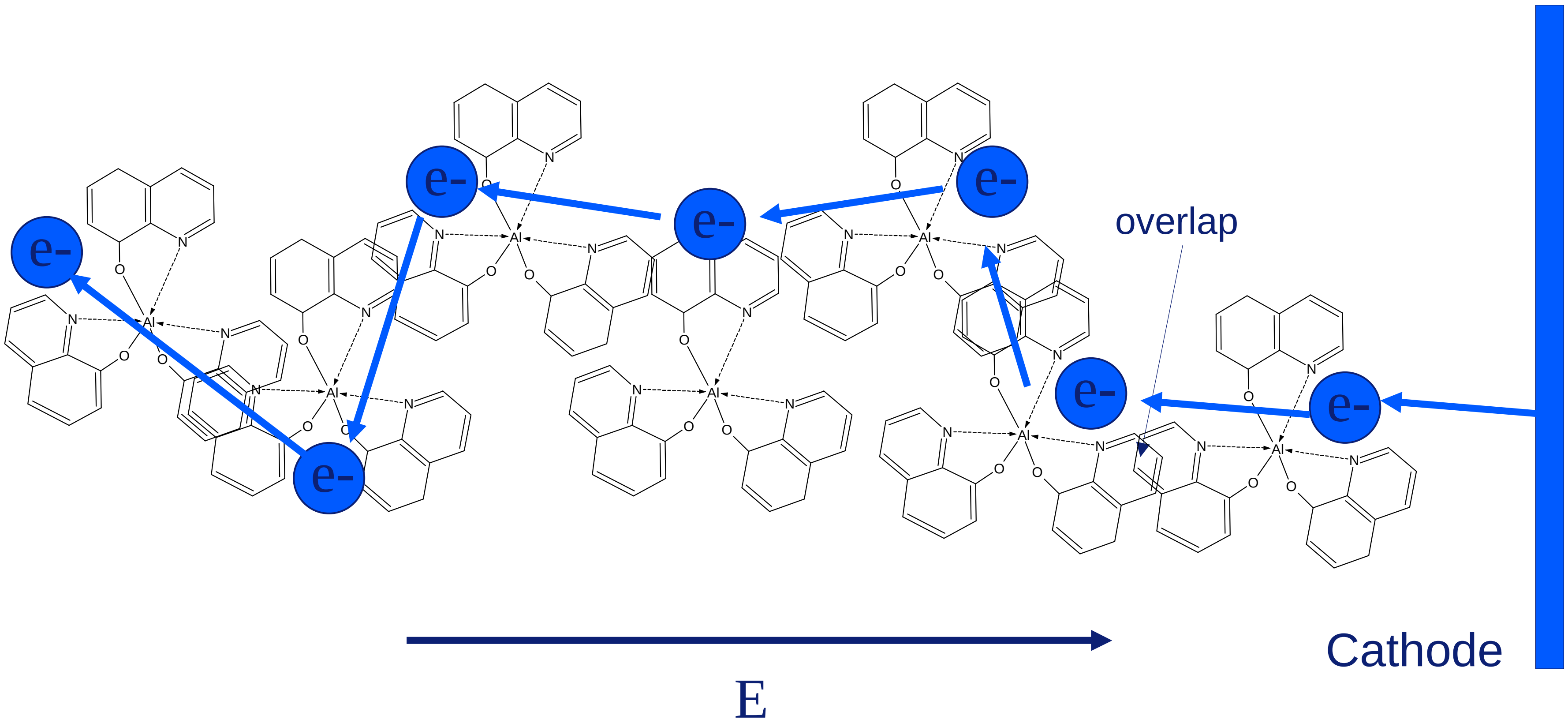
OLED fundamentals: charge transport (holes)



Hole transport = oxidation of the molecules

overlap of molecular orbitals required!

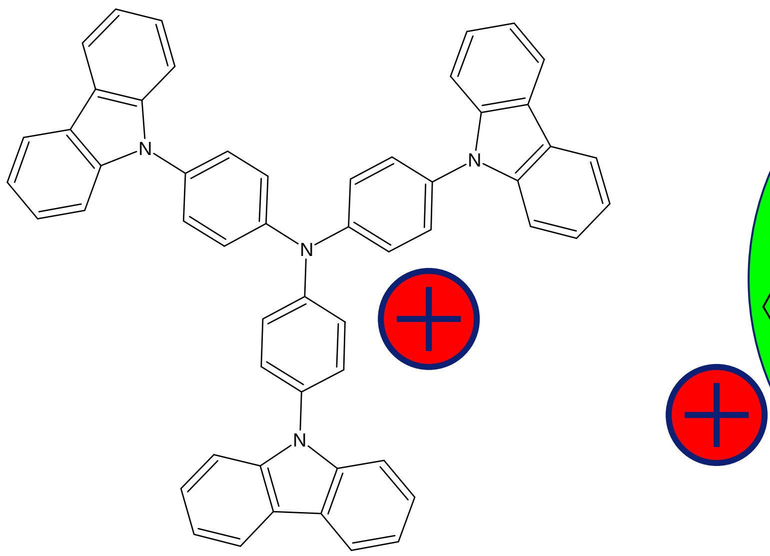
PHILIPS OLED principles: charge transport (electrons)

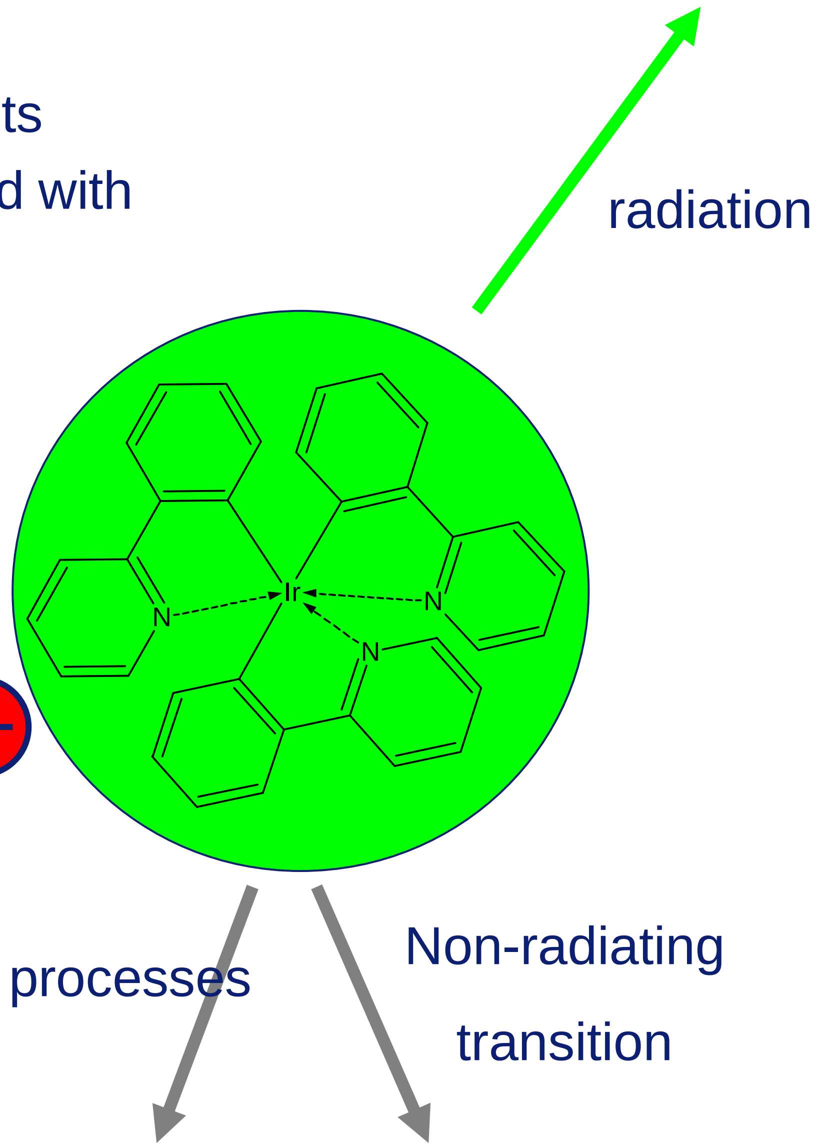


electron transport = reduction of the molecules

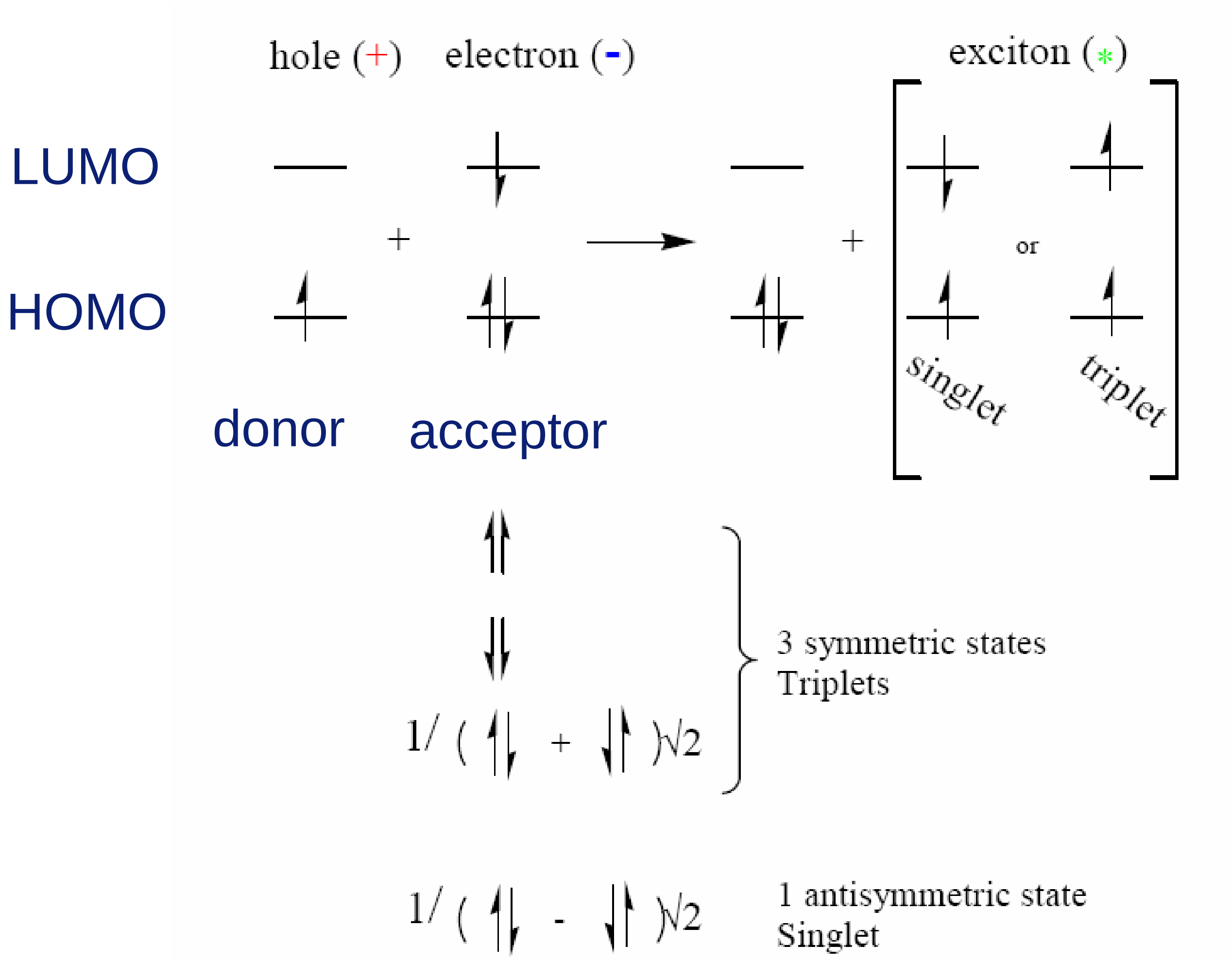
OLED principles: charge recombination

Counter-propagating currents
meet in the emission layer doped with
ca. 8% $Ir(ppy)_3$



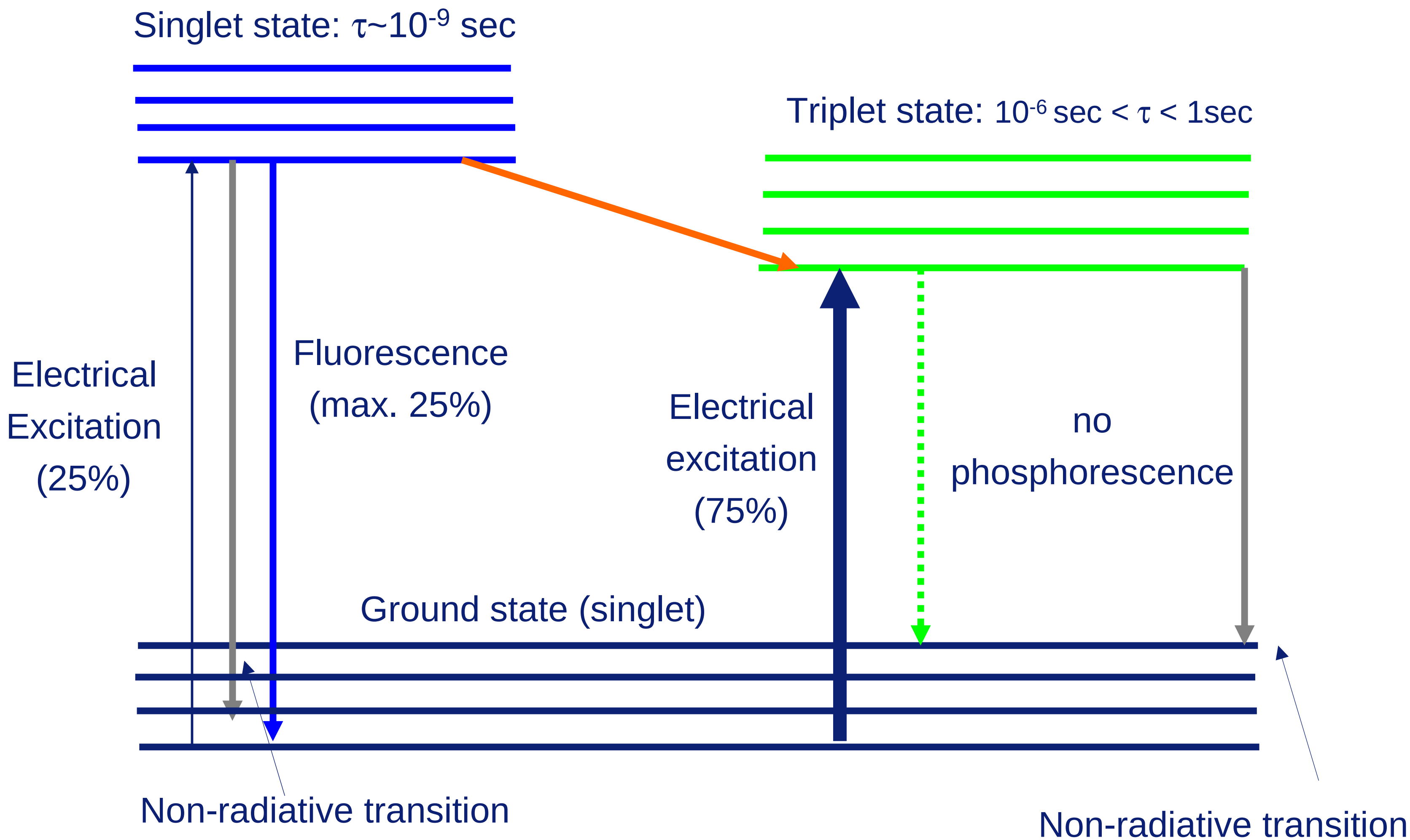


Electroexcitation

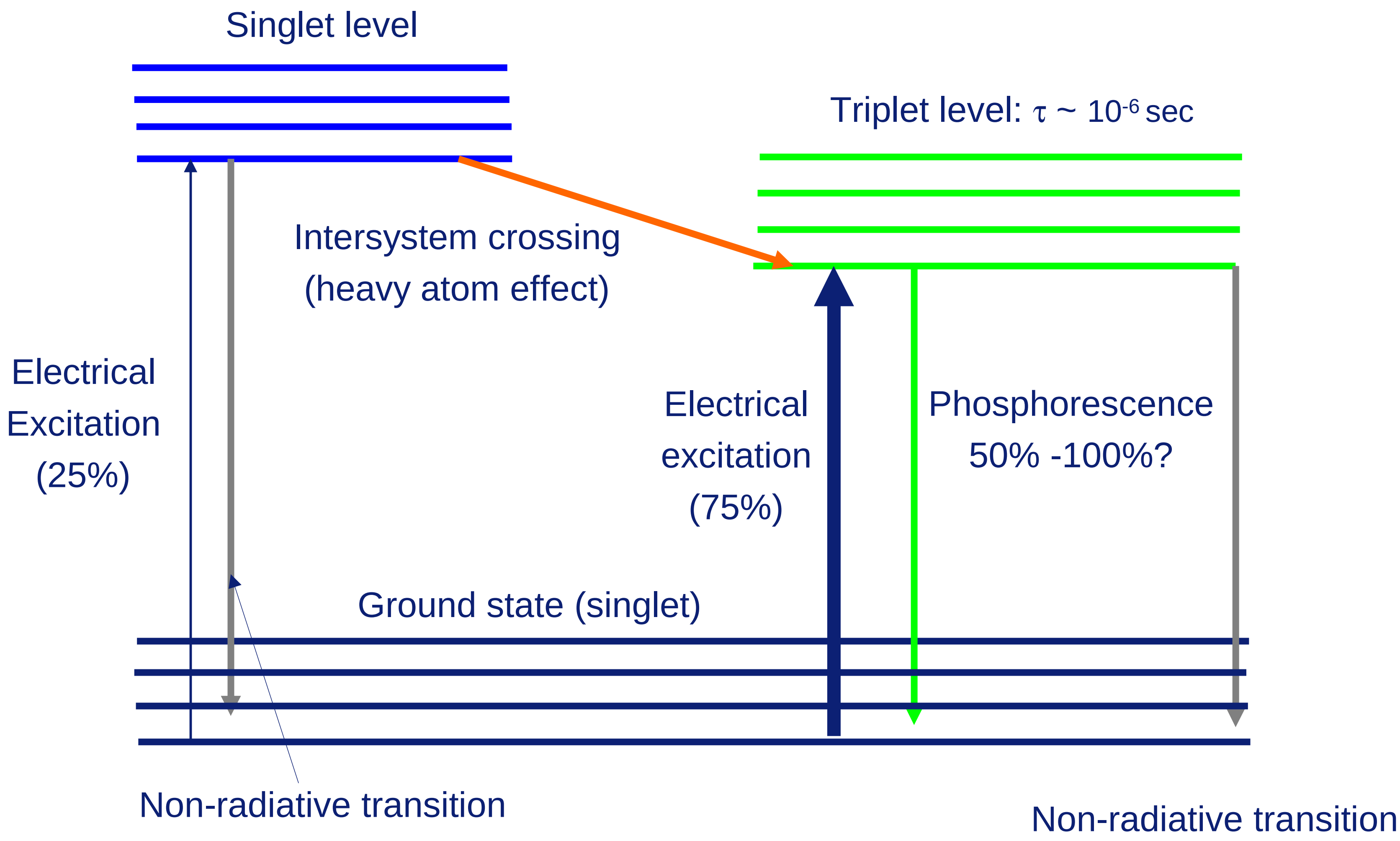


Electroexcitation populates directly and preferably the Triplet state

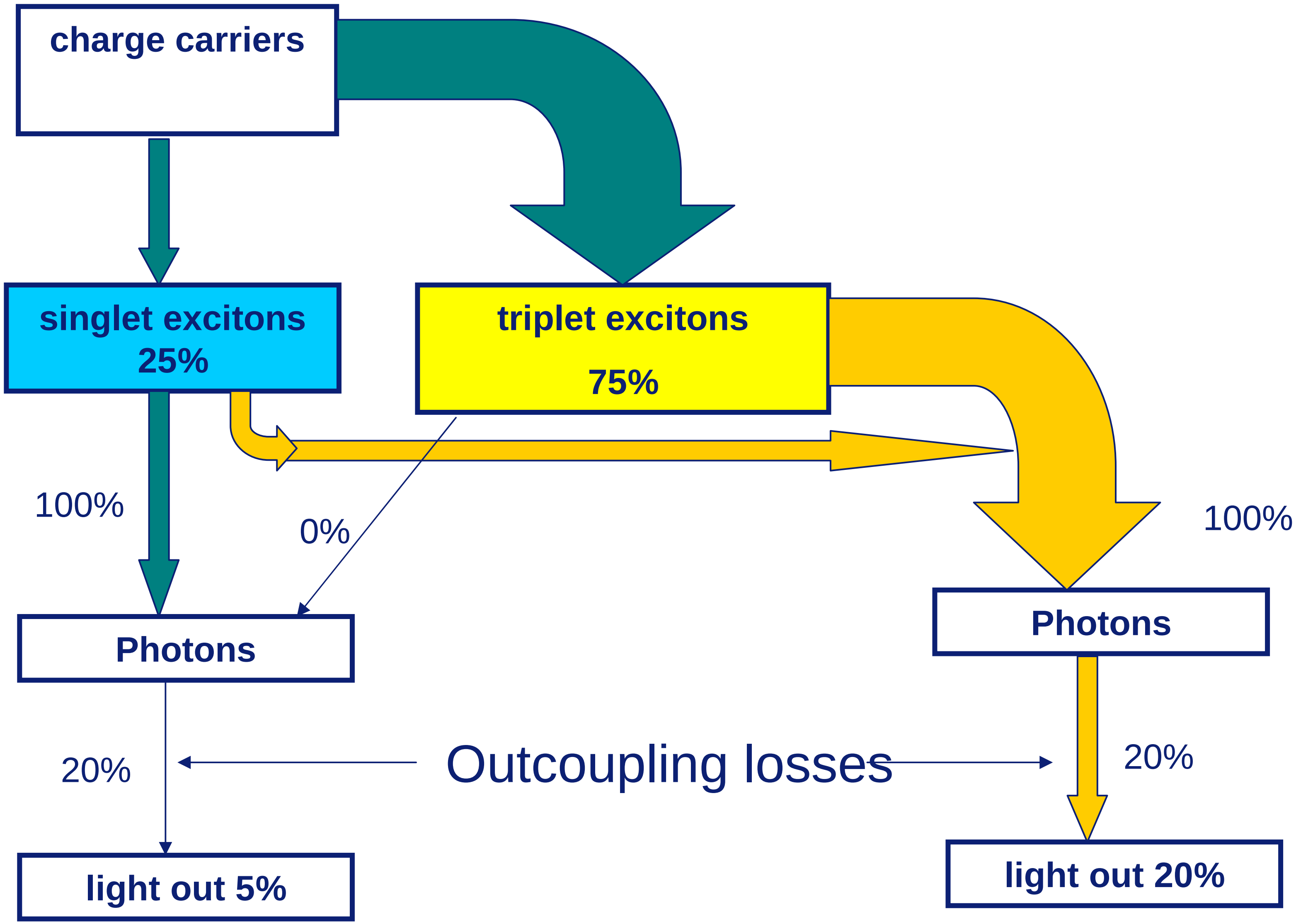
PHILIPS Fluorescent emitters



Phosphorescent emitters



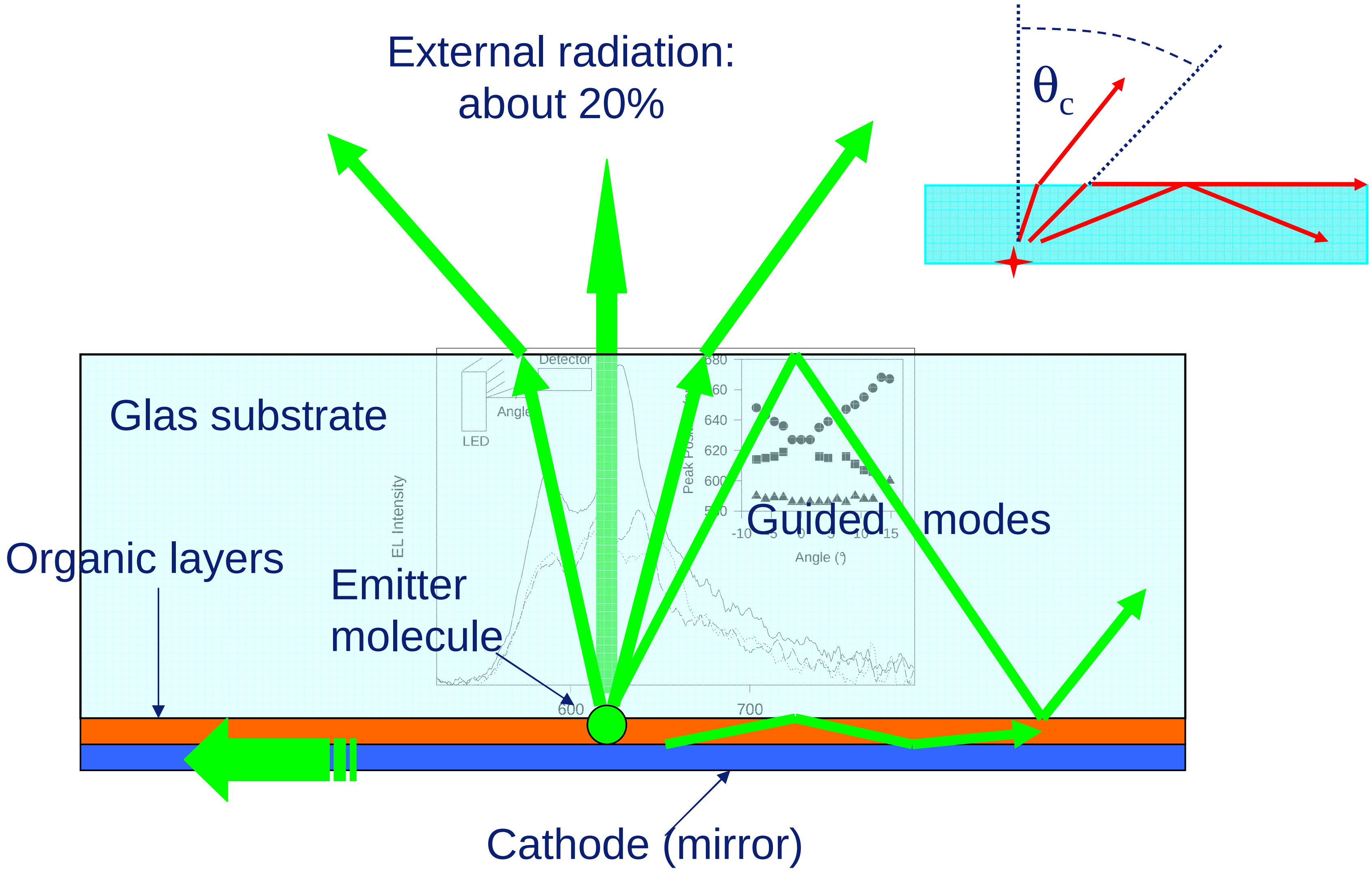
OLED principles: losses



Fluorescent emitters

Phosphorescent emitters

PHILIPS OLED fundamentals: light outcoupling



Light outcoupling

Light outcoupling structures

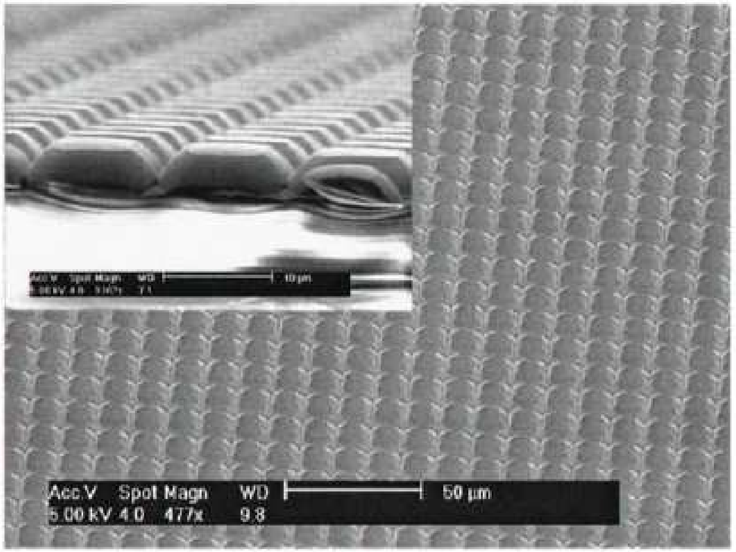
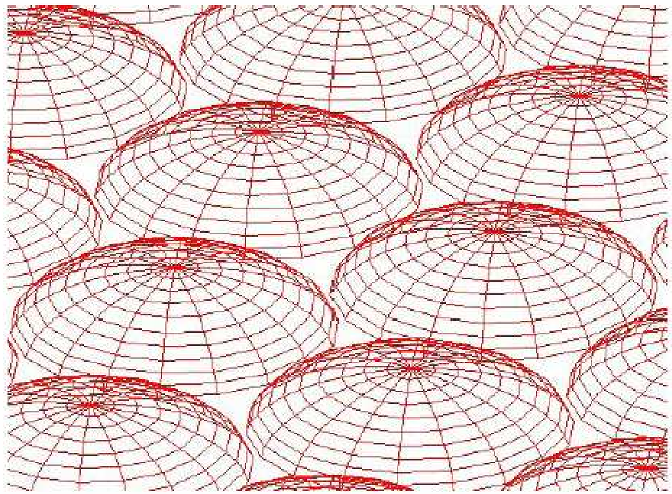
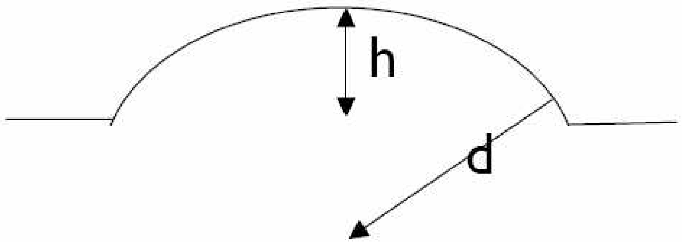
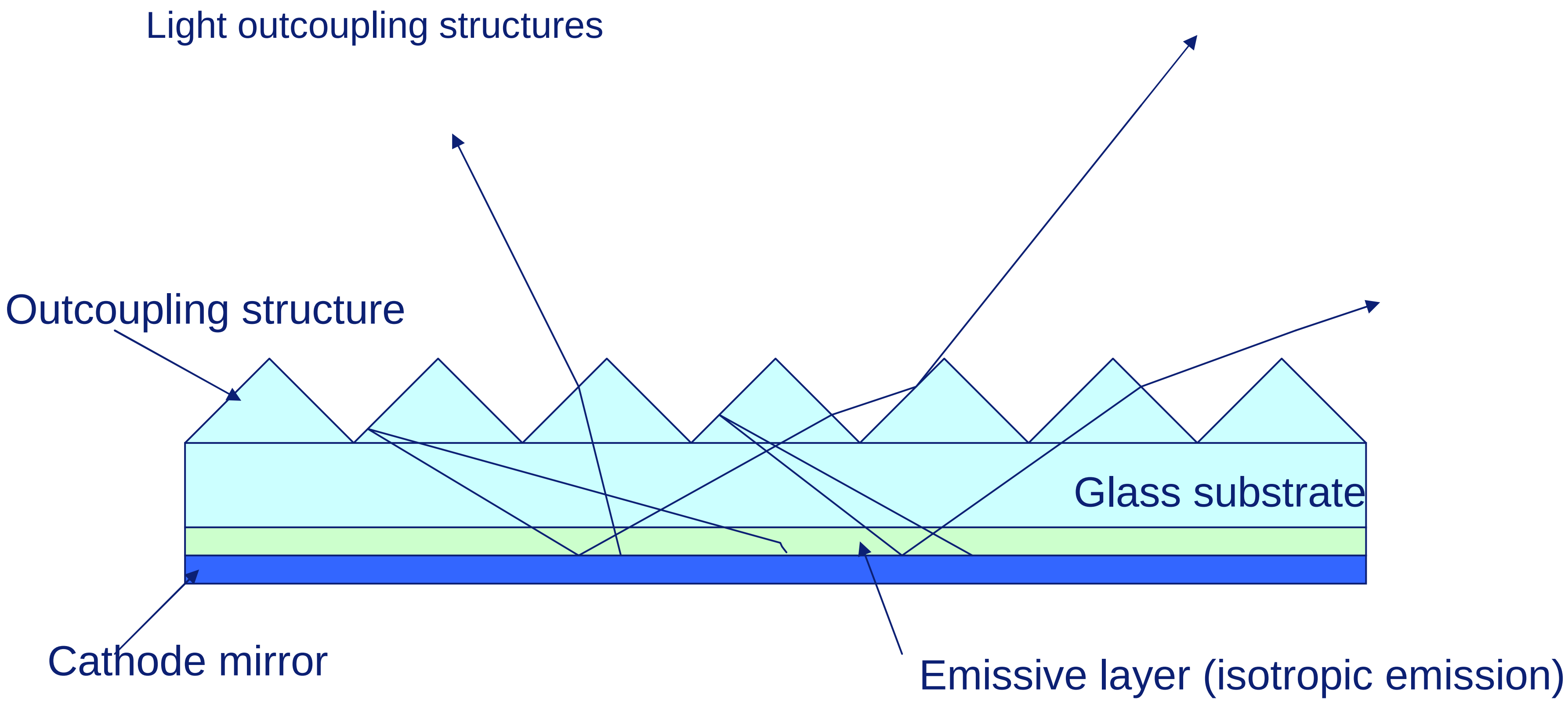


FIG. 3. SEM of a PDMS microlens array fabricated from the mold shown in Fig. 2. The detailed side view of the lenses (inset) shows that the PDMS accurately images the mold shape.





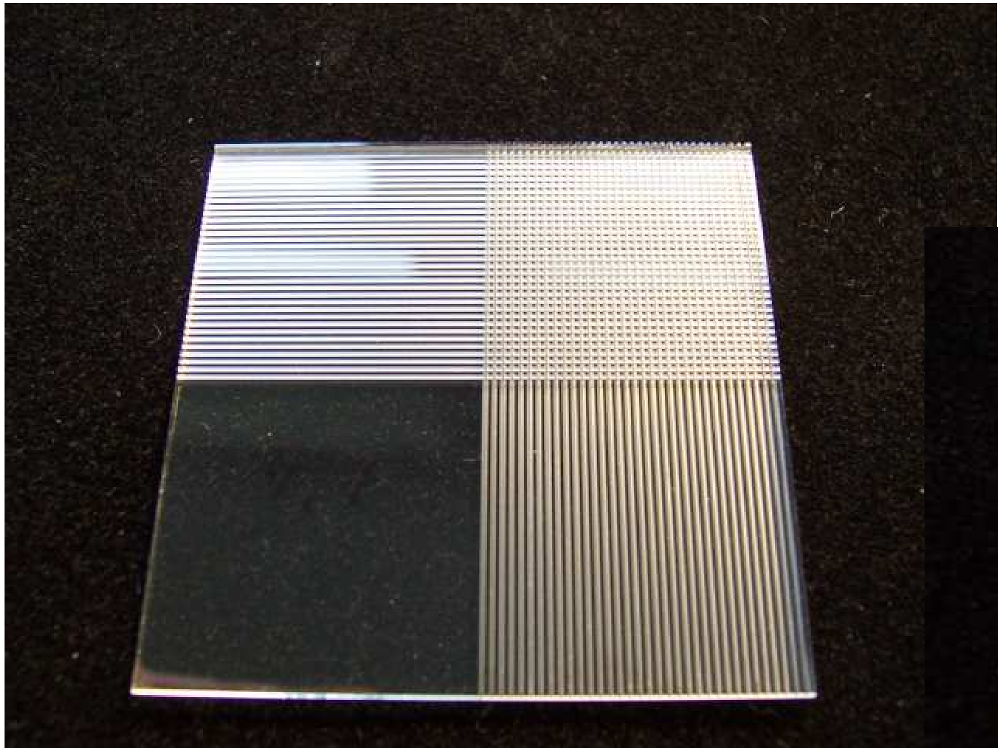
Light outcoupling

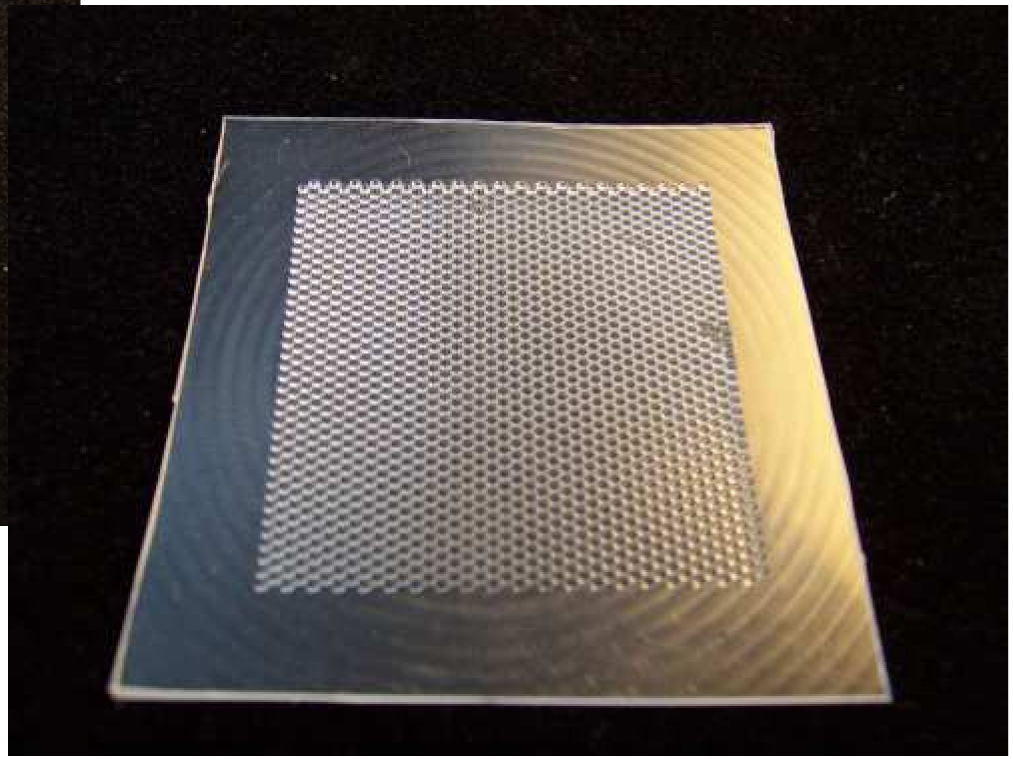


- The outcoupling structures randomize the light ray directions
- Normally, less than 50% of the light entering the glass can escape
- Optimised systems can increase this figure to about 80%

Light outcoupling

Light outcoupling structures: pyramids and lenses





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OLED fundamentals: summary

- Semiconductor band model
- Charge injection from metallic contacts into organic glass
- Charge transport due to hopping
- E-field driven chain reaction: oxidation or reduction
- High electric fields required
- Recombination pumps individual molecule
- Electroexcitation pumps 75% triplet, 25% singlet
- Photoexcitation pumps 100% singlet, triplet only via intersystem crossing
- Triplet emitter needed for high efficiency
- a lot of light is lost in the device and not coupled out (up to 80%)

Mainstream

- Fluorescent emitters (R,G,B)
- Ir-complexes (R,G,B) (lifetime issues with blue)

Special cases

- Eu^{3+}, Tb^{3+} complexes
- Gd^{3+} complexes

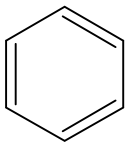
Organic dye molecules: the fundamentals

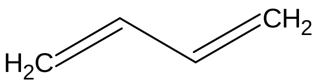
Focus on small molecules exclusively!!

Interaction between photons and molecules requires easily moveable electrons: i.e. the π-electrons of double bonds

Conjugated double bonds are needed for larger π-electron systems

Aromatic systems





High energy limit: hν > bond energy

Low energy limit: thermal stability

Luminescence between 300 and 900 nm

PHILIPS Organic dye molecules: the states

Singlet states

Triplet states

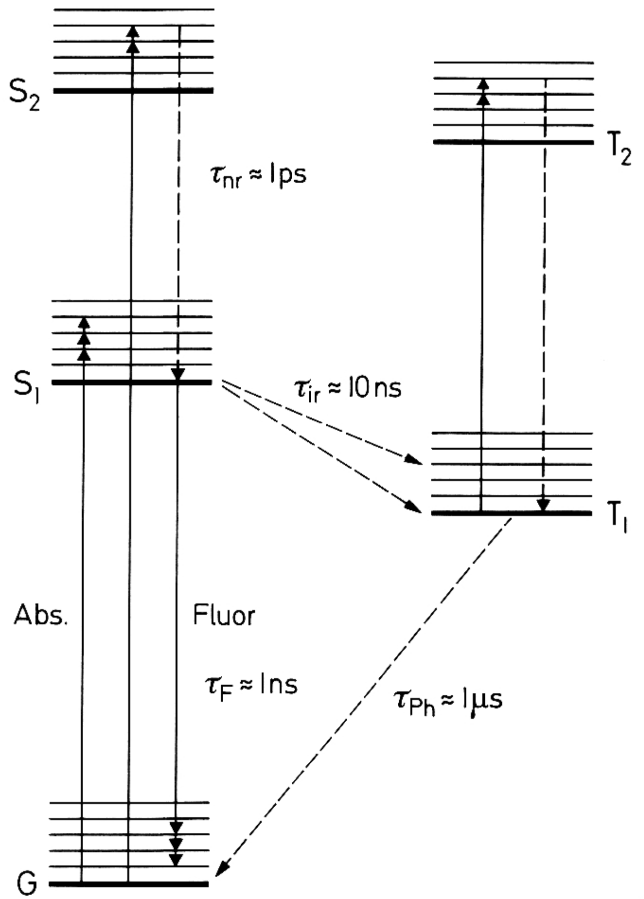


Fig. 1.14. Eigenstates of a typical dye molecule with radiative (solid lines) and non-radiative (broken lines) transitions

F. P. Schäfer, Dye Lasers, Springer 1973

Organic dye molecules

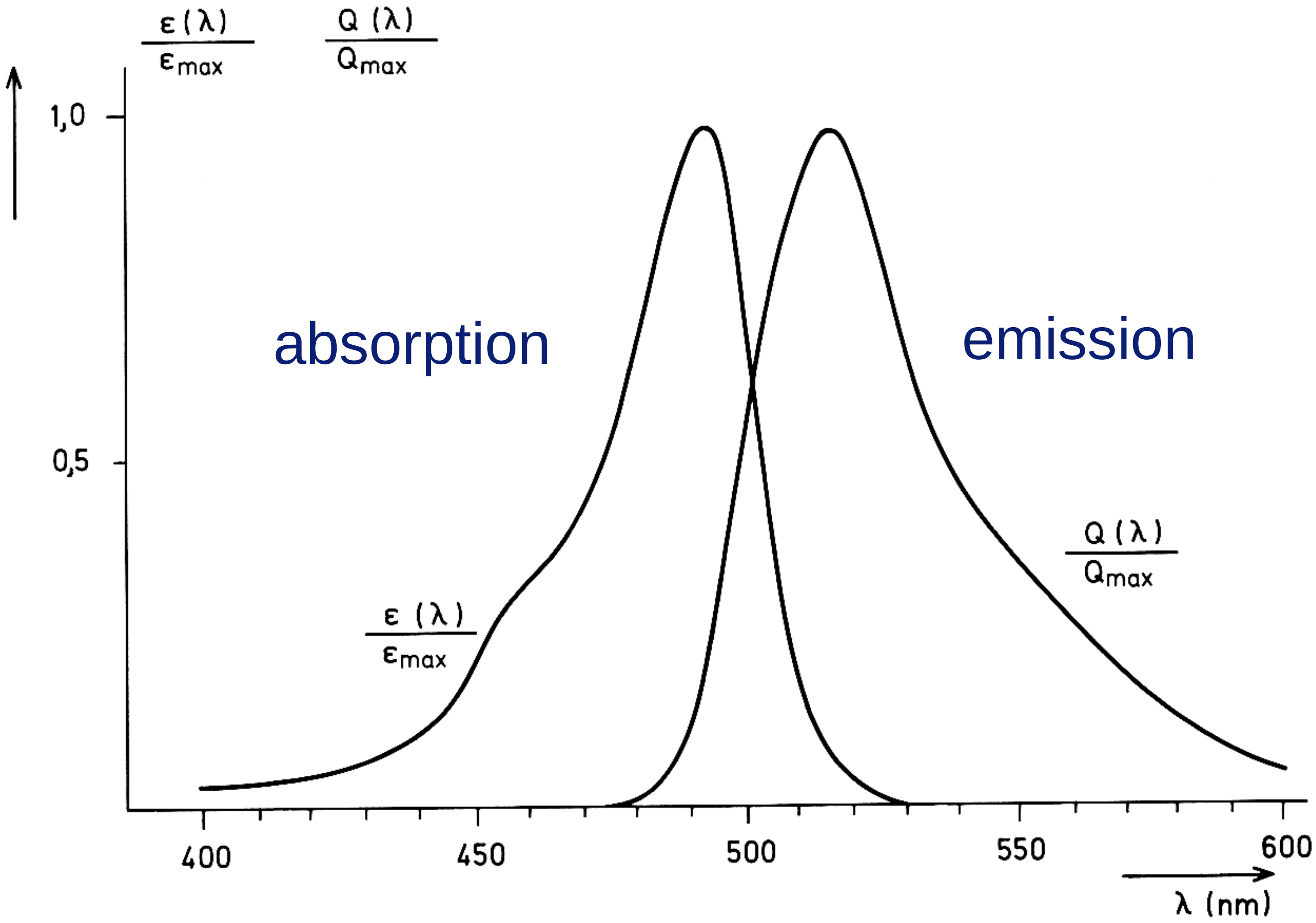
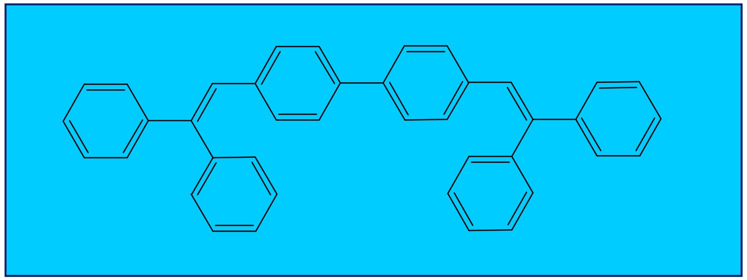


Fig. 1.7. Absorption spectrum, $\varepsilon(\lambda)/\varepsilon_{max}$, and fluorescence spectrum, $Q(\lambda)/Q_{max}$, of a typical dye molecule (fluorescein-Na in water)

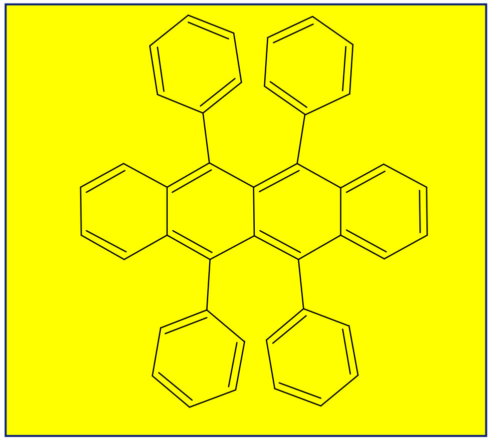
F. P. Schäfer, Dye Lasers, Springer 1973

Fluorescent emitters: examples

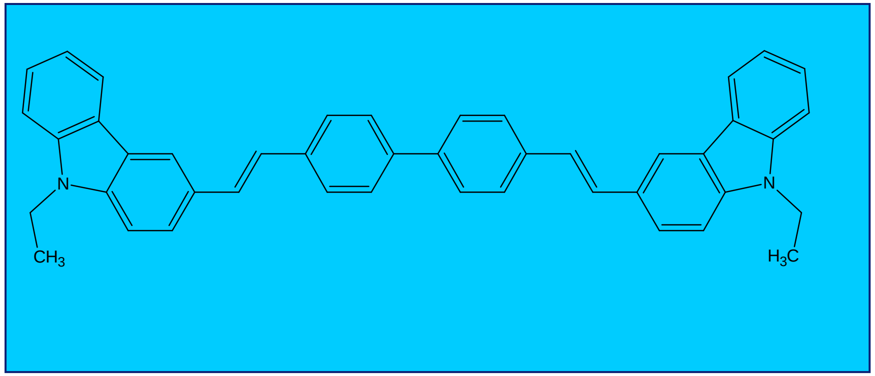
DPVBi



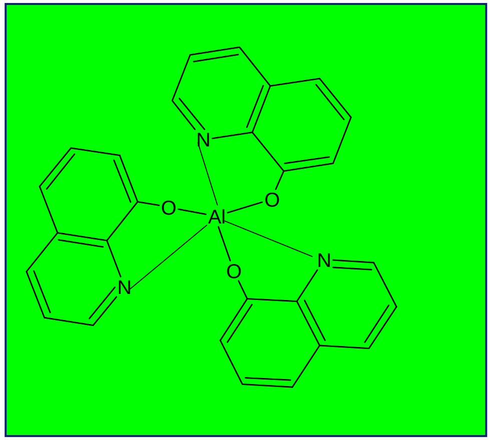
Rubrene



BCzVBi

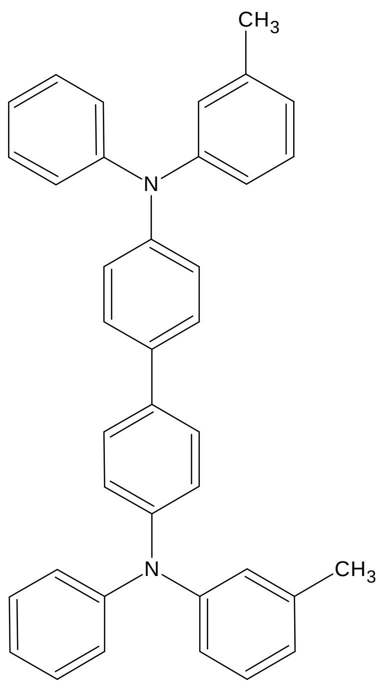


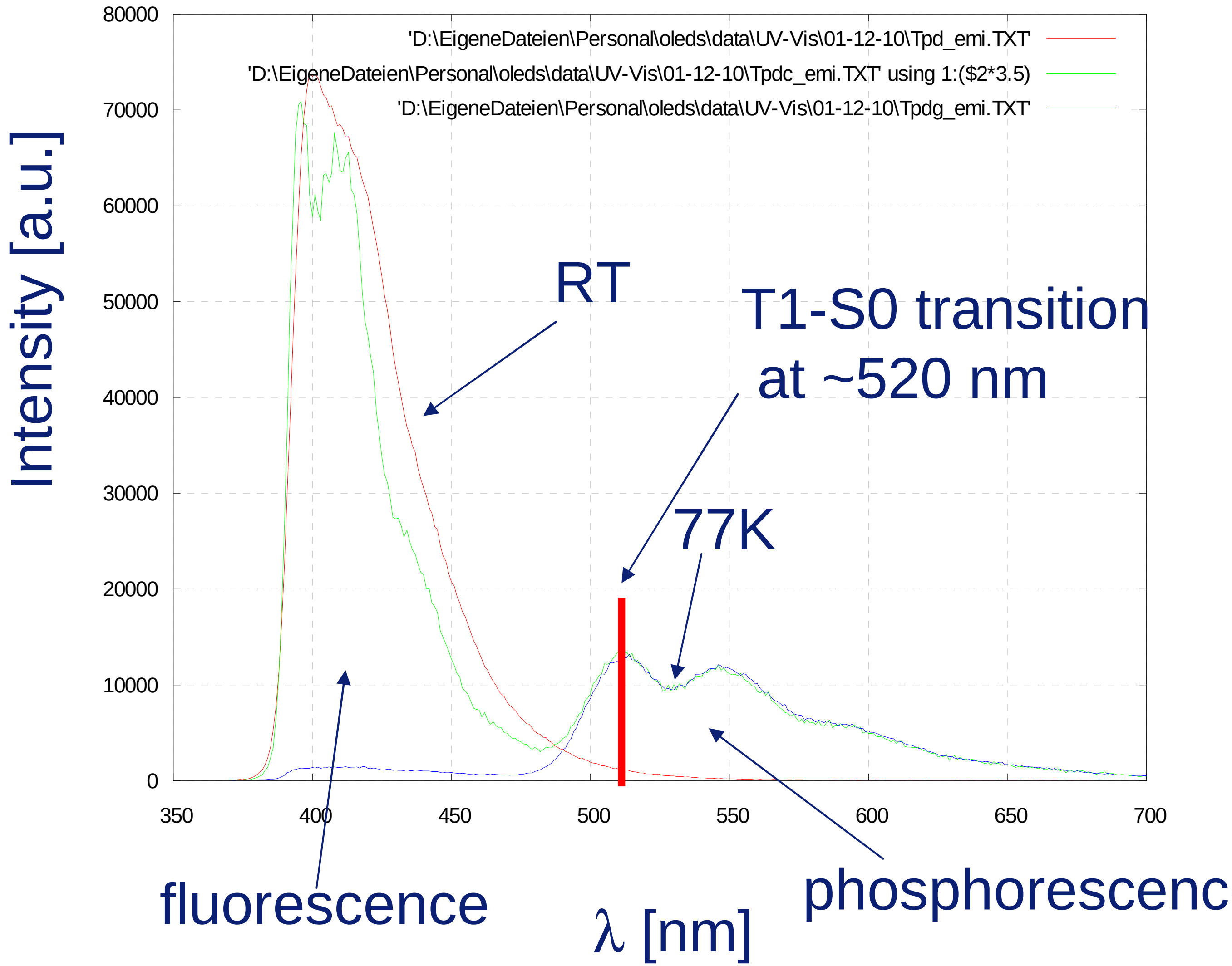
ALQ_3



Phosphorescence at 77K: TPD

Hole conductor

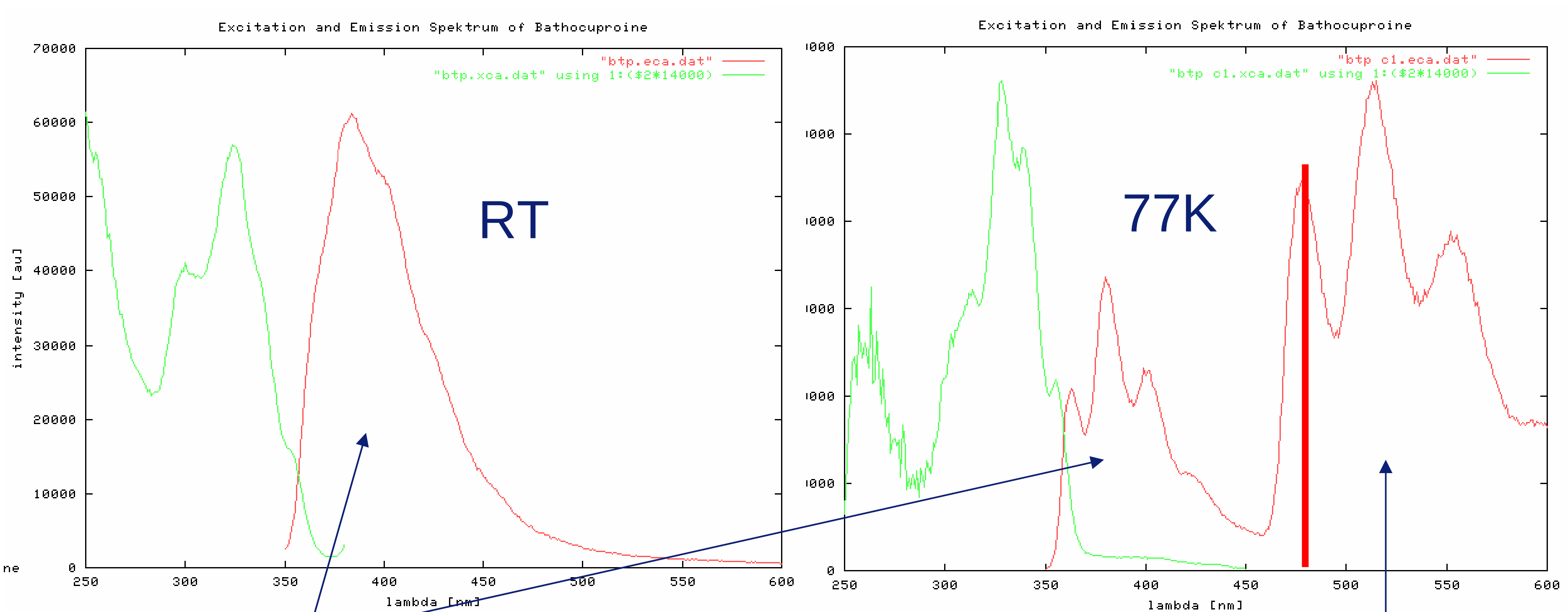




Solvent: m-THF

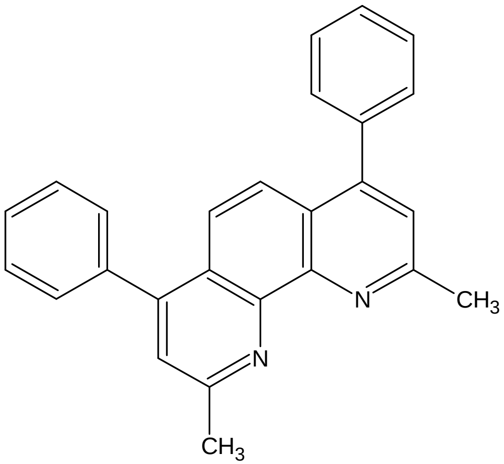
PHILIPS Phosphorescence at 77K: BCP (Bathocuproine)

Electron conductor



fluorescence

phosphorescence



T1-S0 transition at ~480 nm

Solvent: m-THF

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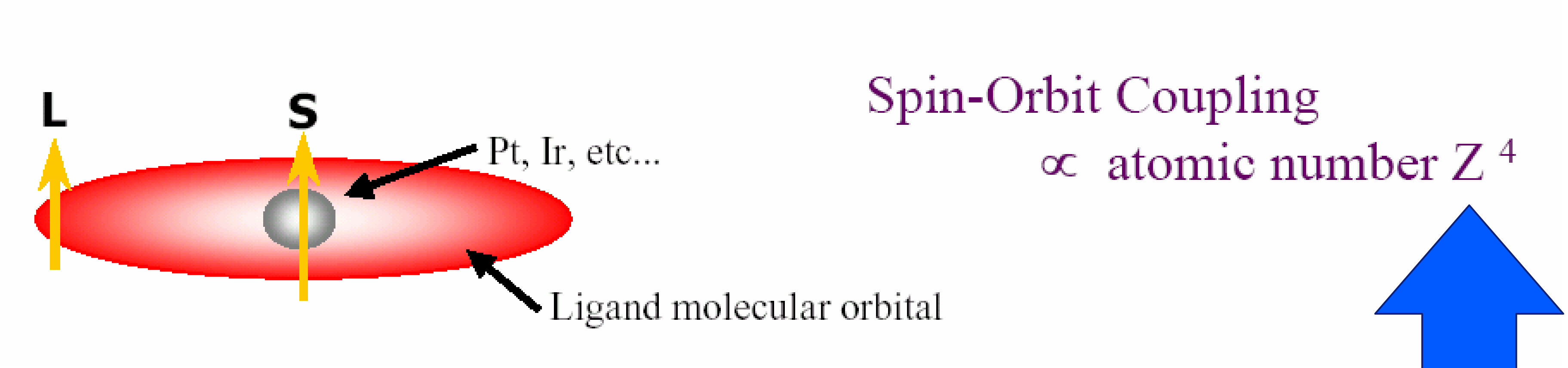
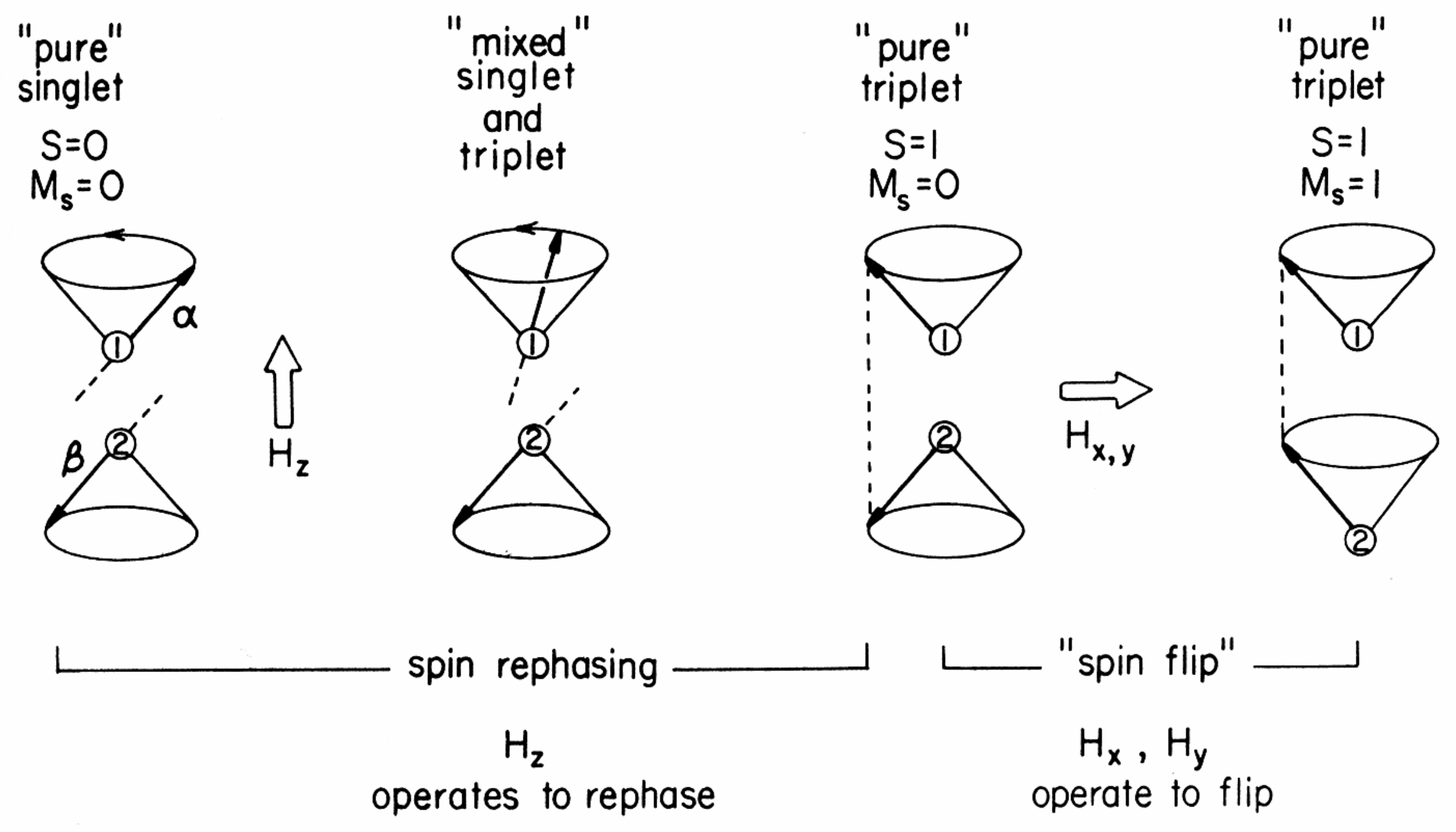
Complexes or metalorganic compounds with heavy metal atoms



Enhances the S-T transitions:

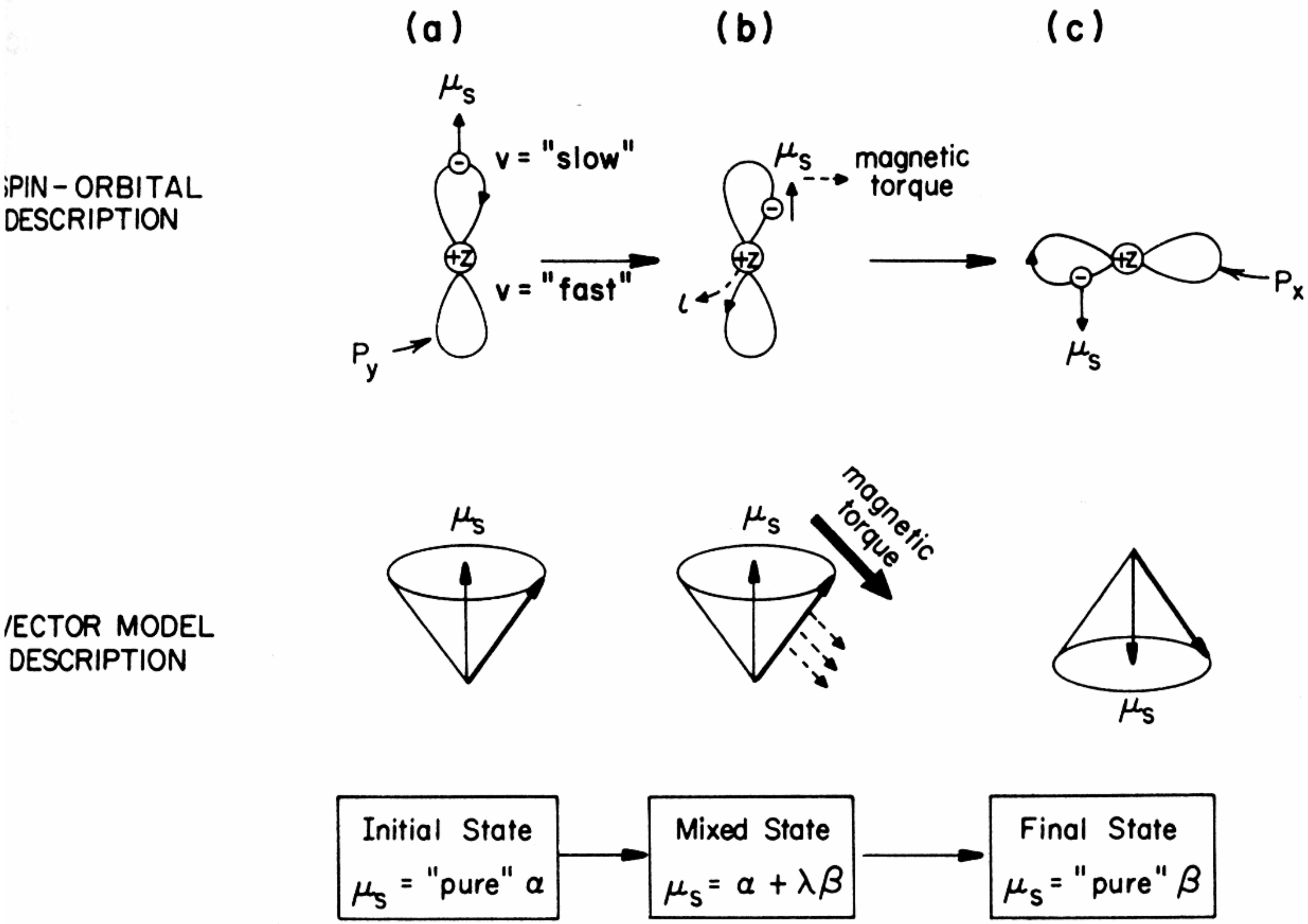
- Intersystem crossing
- phosphorescence

Spin-orbit coupling



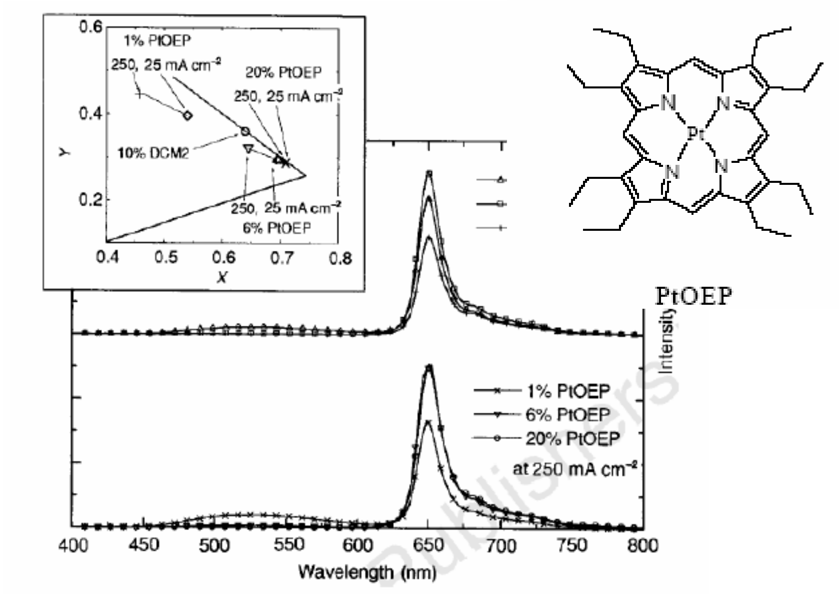
N. J. Turro, Modern Molecular Photochemistry, University Science Book, CA, 1991

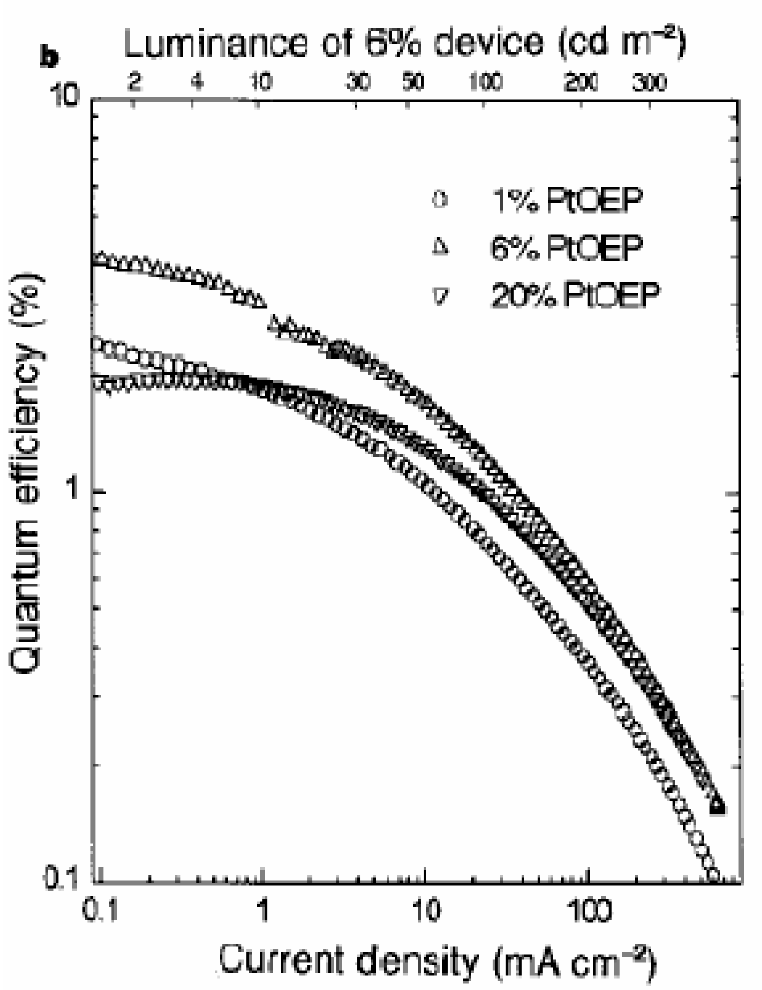
Spin-orbit coupling: a simple model



N. J. Turro, Modern Molecular Photochemistry, University Science Book, CA, 1991

First efficient phosphorescent OLED: Pt complex





ITO/a-NPD/Alq3:6% PtOEP/Alq3/Mg:Ag

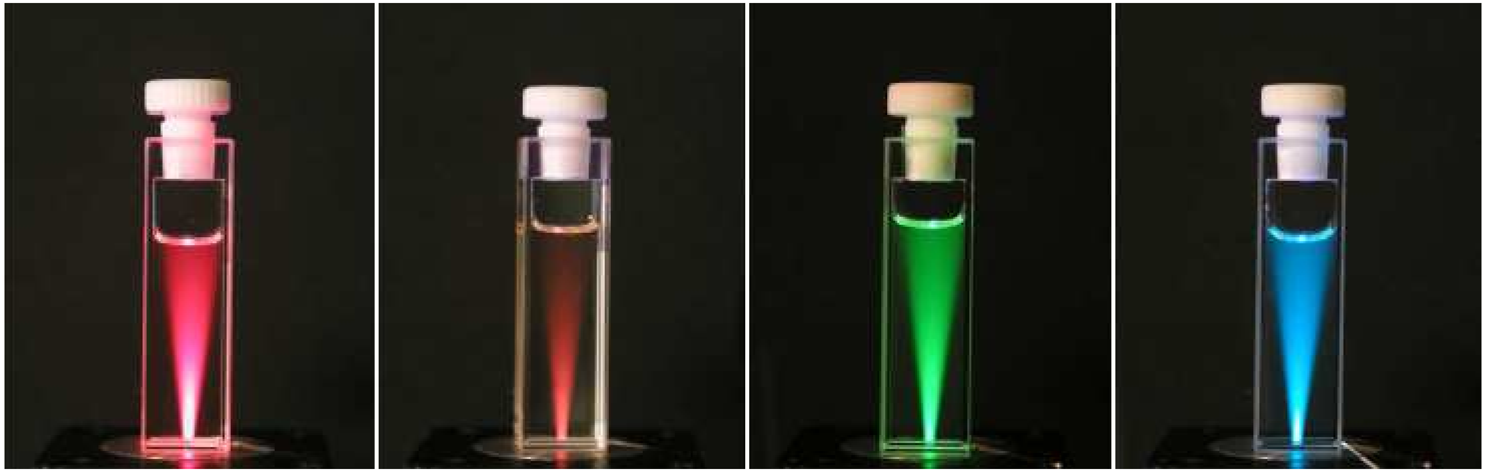
η ext: 4%

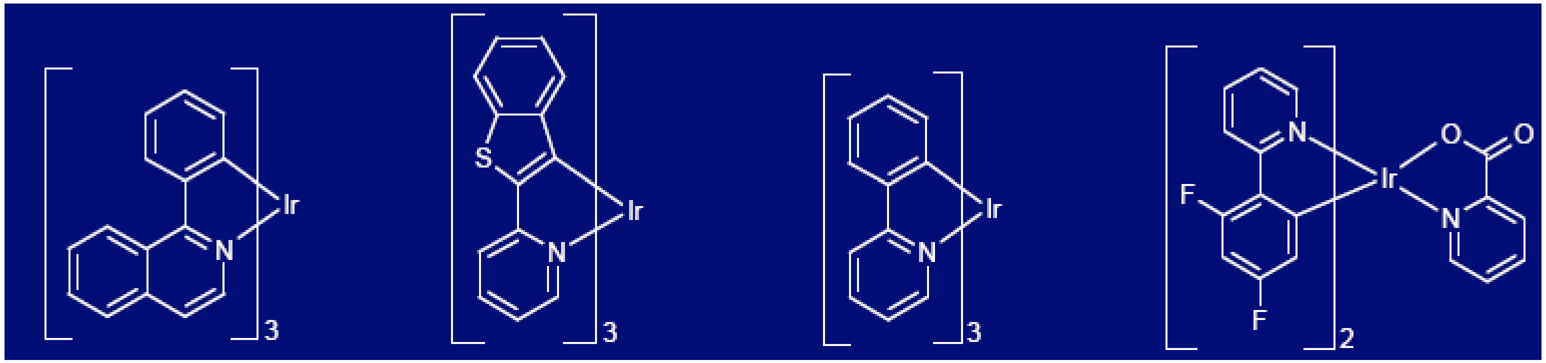
η int: 23%

Power efficiency : (8.9±0.9) lm/W

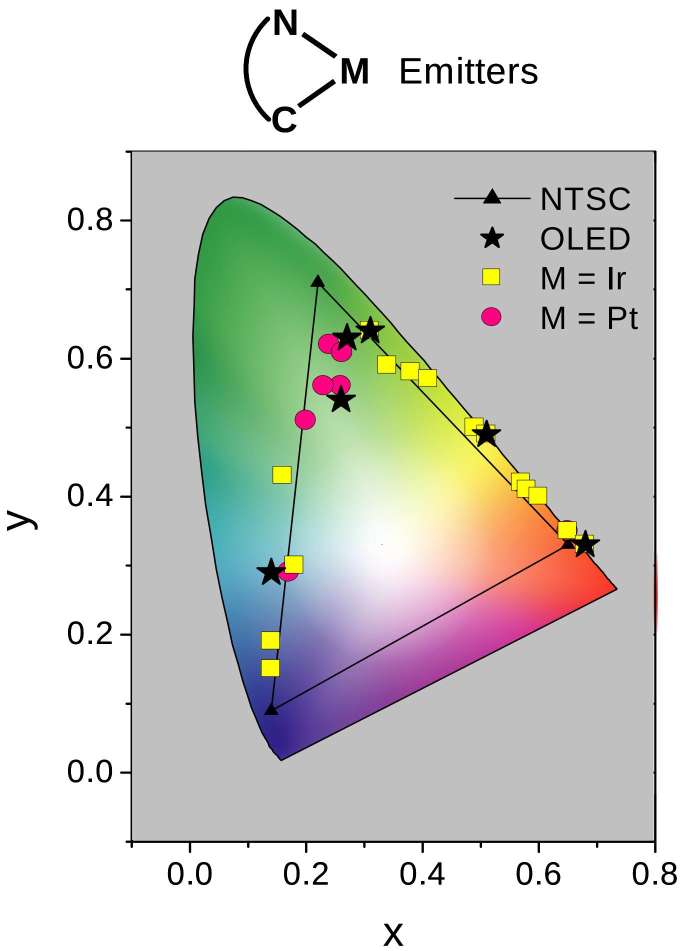
M. A. Baldo *et al*. Nature, **395**, 151 (1998)

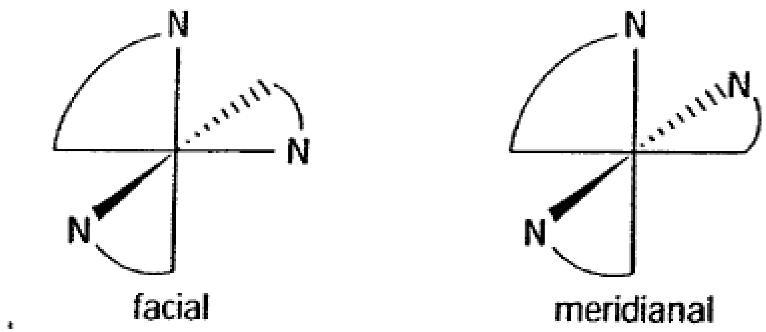
Iridium based triplet emitters





Source: BASF

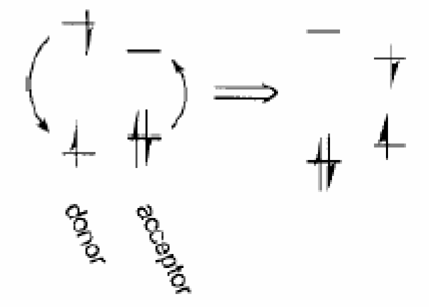




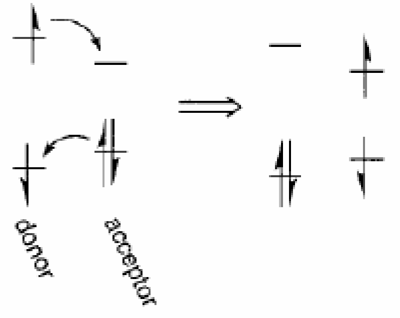
Radiative lifetimes: ~ 1 μ sec

PHILIPS Exciton energy transfer

- Förster energy transfer: A Coulombic interaction between the host exciton(donor) and the dopant:
- dipole-dipole coupling
- fast process
- long distant process (up to 10 nm)
- Singlet energy transfer



- Dexter transfer: An electron-exchange interaction between the host exciton and the dopant
- requires electron exchange
- short distant process (1.5-2.0 nm)
- Triplet energy transfer



PHILIPS Iridium complexes in OLEDs: matrix requirements I

Iridium complex

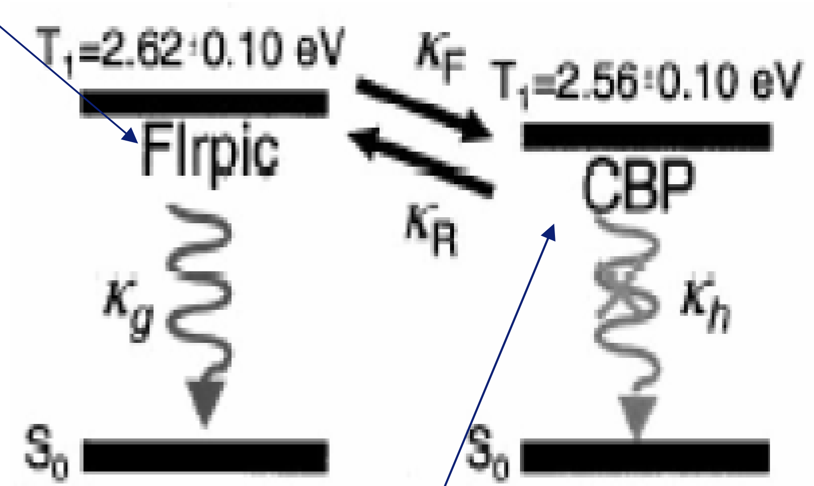
Firpic in CBP matrix

C. Adachi *et al*. APL, 79, 2082 (2001)

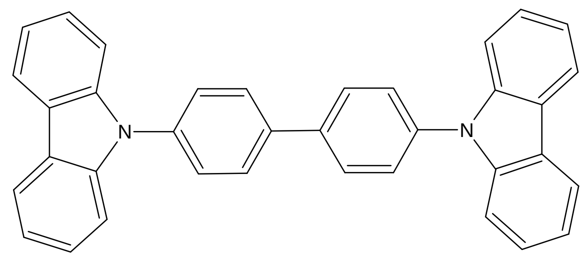
ITO/ CuPC/ α-NPD/ CBP:6% FIrpic/ BAlq3 /LiF/Al

η ext: (5.7±0.3)%

Power efficiency : (6.3±0.3) lm/W



Matrix material (hole conductor)



Firpic in CDBP matrix

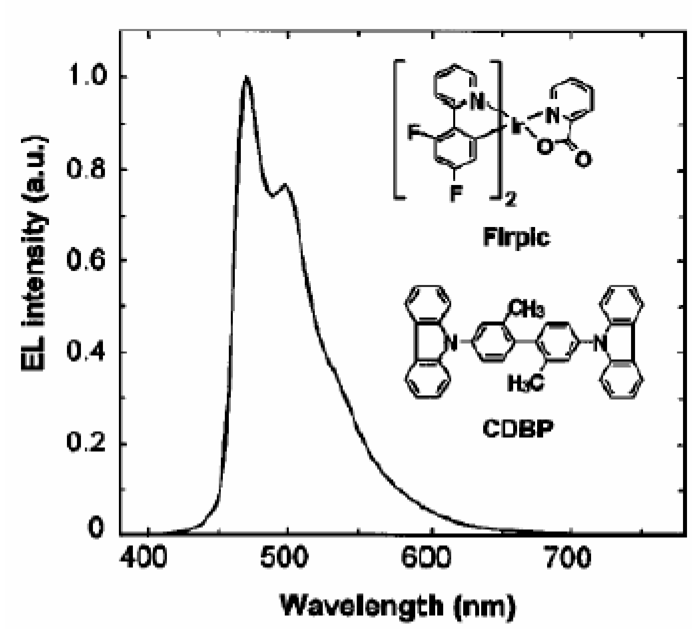
S. Tokito *et al*. APL, 83, 569 (2003)

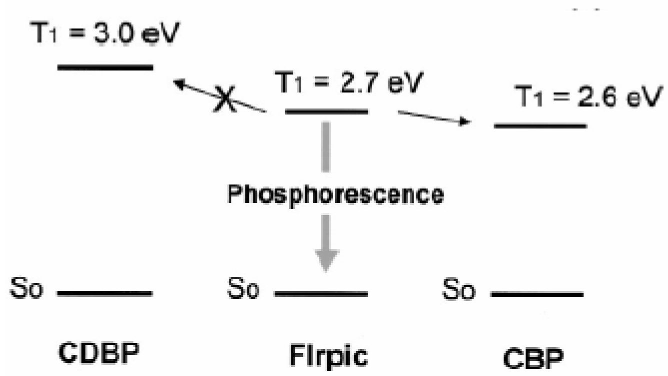
ITO/ PEDOT/ α-NPD/ CDBP:3% FIrpic/ BAlq3/ LiF/ Al

η_{ext}:10.4%

Current efficiency : 20.5 cd/A

Power efficiency : 10.5 lm/W





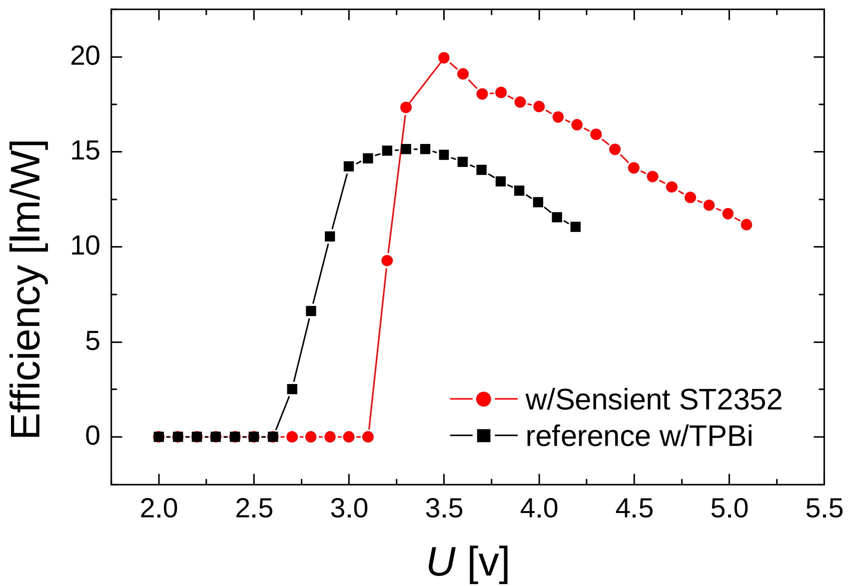
Firpic in new matrix

ITO/ MTDATA:F4-TCNQ/ MTDATA/
NTMM:9% FIrpic/ ST2352/ LiF/ Al
η_{ext}:14.5% max

Current efficiency : **31.5 cd/A**

Power efficiency : **23 lm/W**

NTMM:
T_1 = 2.9 eV,
HOMO = -5.35 eV
ST2352:
T_1 = 2.81-2.85 eV,
HOMO = -6.62 eV



- Summary
- Fluorescent emitters are well researched, but limited because of their internal QE of 25%
- Ir-complexes are by far the best studied and most efficient phosphorescent emitter systems known with IQE up to 100%
- Efficiency will deteriorate dramatically if Dexter (triplet) energy transfer to matrix molecules is possible
- For blue triplet emitters, new matrix molecules with a high T_1 level are required

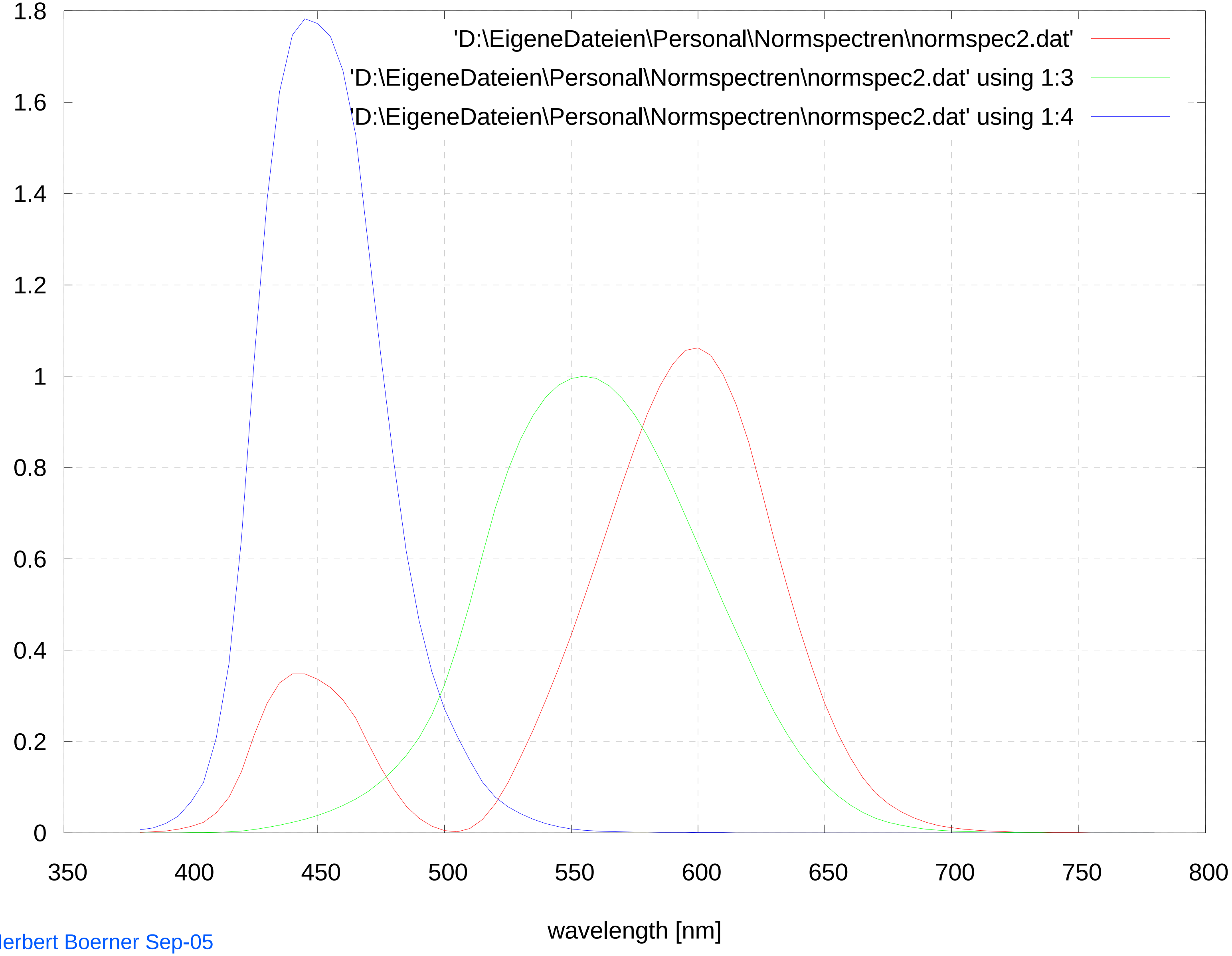
(Artificial) lighting fundamentals

- Radiometric and photometric units
- Color and color rendering
- Conventional light sources:
  - incandescent
  - fluorescent

Spezifications of lightsources

Quantity	description	unit
Energy efficiency	Visible radiation flux per electrical power	%
Efficacy	Radiation power per electrical power	lm/W
Color point	Coordinates in the CIE diagram	x,y
Color temperature	CIE coordinates on black body line	K
Color rendering	Comparison of color impression from test charts	N.A.

Eye color response



Radiation measurement

- *Units for power (proportional to number of photons per time unit):*
- Flux $\Phi_e = dW/dt$ [J/s = W]
- Radiation density $D_e = d\Phi_e/dA$ [W/m^2]
- Spectral density $L_e = dD_e/d\lambda$ [W/m^{2}nm]

- Example: Sun-Earth: $E_{es} = 1.35$ kW/m^2 (solar constant)

Calculating # of photons: $E = h\nu = hc/\lambda$ und $h\nu_{550} = 4{*}10^{-19}$ J
$\Rightarrow$ 1 W = $2.5{*}10^{18}$ Photons/sec

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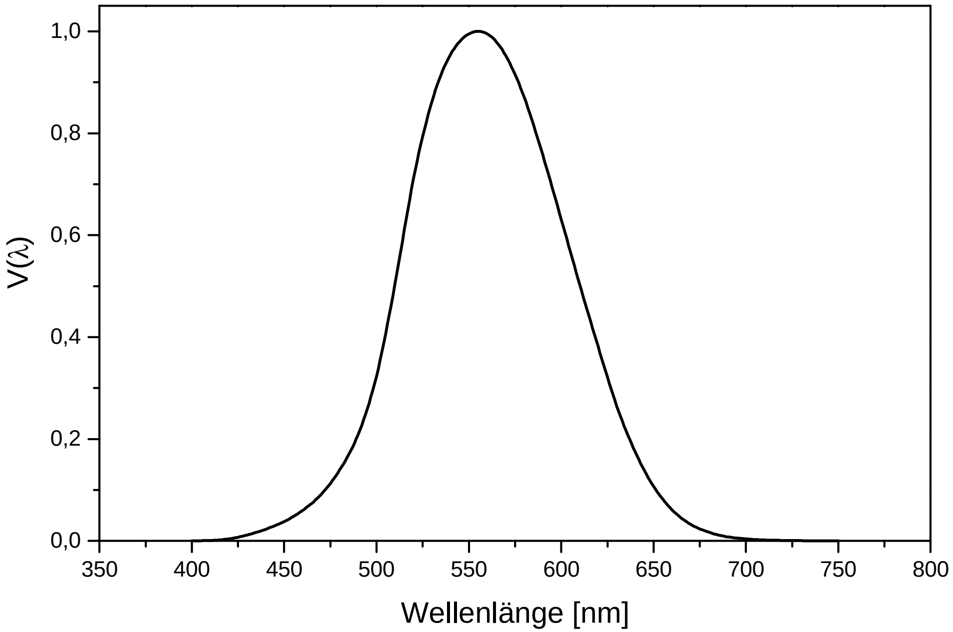
Photometric units

Units related to eye-sensitivity of humans



$$\Phi = K_{\max} \int_{380}^{780} V(\lambda)\Phi_{\varepsilon}(\lambda)d(\lambda)$$

- Lightflux $\Phi = \Phi e/M_0$ [lm]
- (M_0 = energetic light equivalent
- = 0.00146 W/lm)

- K_{max} = 683 lm/W (bei 555 nm)
- $K(\lambda) = K_{max}V(\lambda)$

- Light power $I = d\Phi/d\Omega$ [cd]
- (Ω = solid angle [sr])

Photometric units

Integral units	Angular units
Light power $\Phi = \Phi_e/M_0$ [lm]	Light flux $I = d\Phi/d\Omega$ [cd]
Illumination $E = d\Phi/dA$ [lux = lm/m^2]	Brightness $L = dI/dA \cos\gamma$ [cd/m^2]

Examples:

Light source	**Brightness [cd/m^2]**
Sun	1.5×10^9
Discharge arc	$2.0 \times 10^8 – 1.0 \times 10^9$
Light bulb (clear)	$2.0 \times 10^6 – 2.0 \times 10^7$
Light bulb (matte)	$5.0 \times 10^4 – 5.0 \times 10^5$
Fluorescent tube	$4 \times 10^3 – 1.4 \times 10^4$
Candle	7.5×10^3
Blue sky	$3 \times 10^3 – 5 \times 10^3$
Moon	2.5×10^3
TV	5×10^2

Energy efficiency

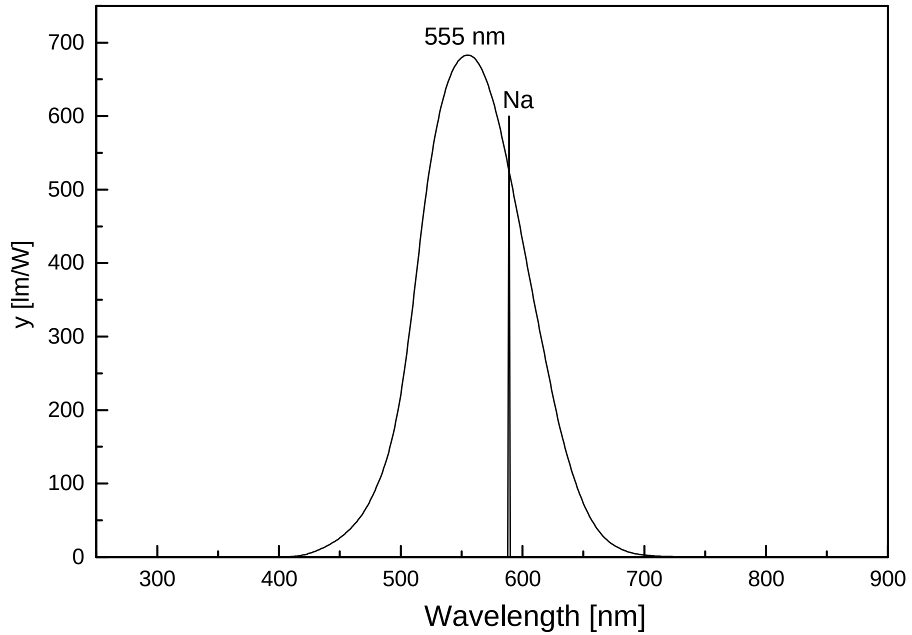
- Definition $W_{h\nu(visible)}/W_{electrical}$ [%]

- Measurement in integrating sphere

Lamp type	Efficiency [%]
Incandescent	5
Halogen	8 - 10
Energy saving (CFL)	16
Hg-High pressure	17
Fluorescent tube	29
Na-high pressure	31
Na-low pressure	40

Light efficacy

Eye sensitivity diagram



- Light efficacy =
- Efficiency* LE (luminous equivalent)

$$LE = \int_{380}^{780} y(\lambda)E(\lambda)d\lambda$$

Example

Na-low pressure	efficiency	40 %
(Emission at 589 nm)	LE	500 lm/W_h
yellow light	Light efficacy	200 lm/W_{el}

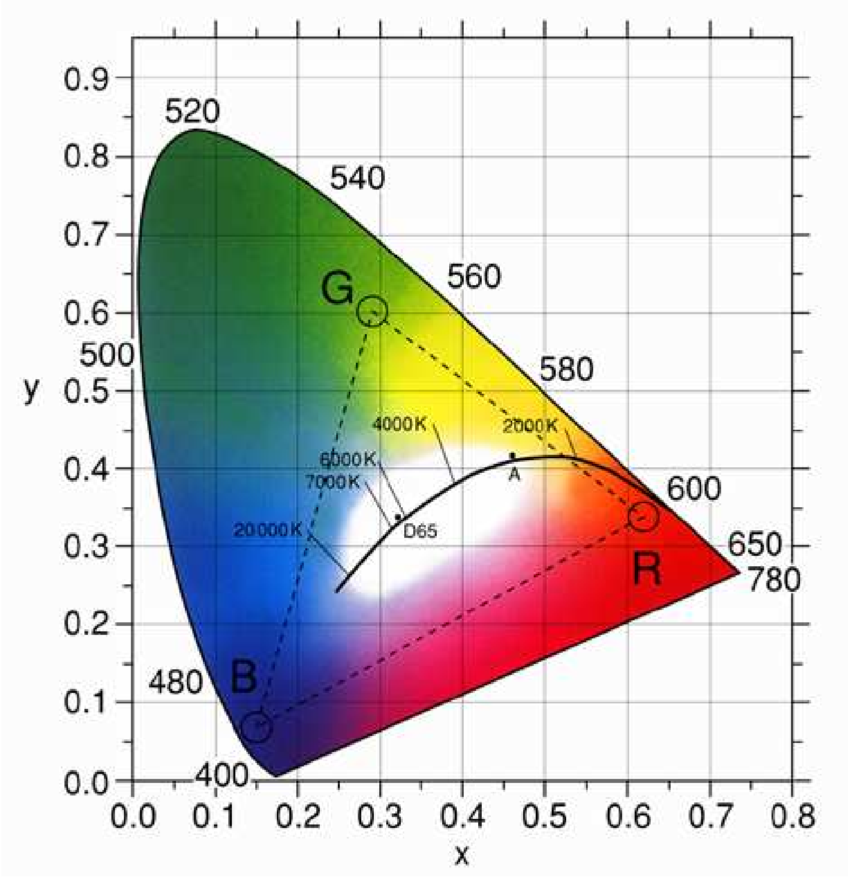
Color point and color temperature

- Color point
- x,y-Coordinates in the
- CIE-color triangle

- Color temperature
- Correlated to the color point of a black body radiator

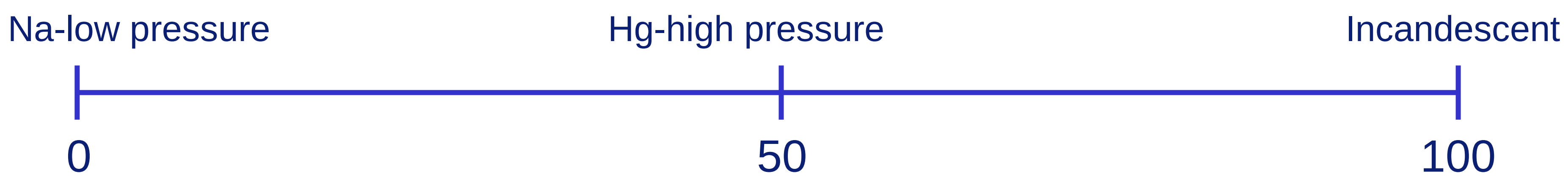
- Incandescent bulb 2700 K
- Fluorescent tube 4000 K
- Daylight 6500 K

C.I.E. System
(Commission Internationale de l'eclairage)

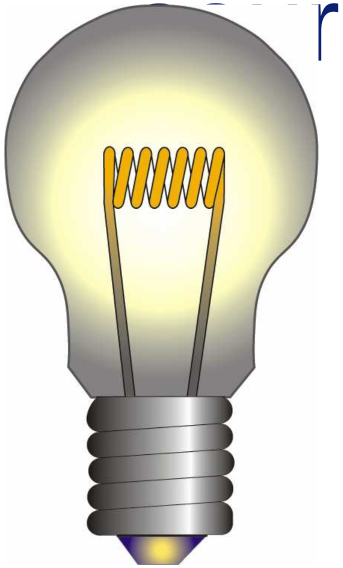


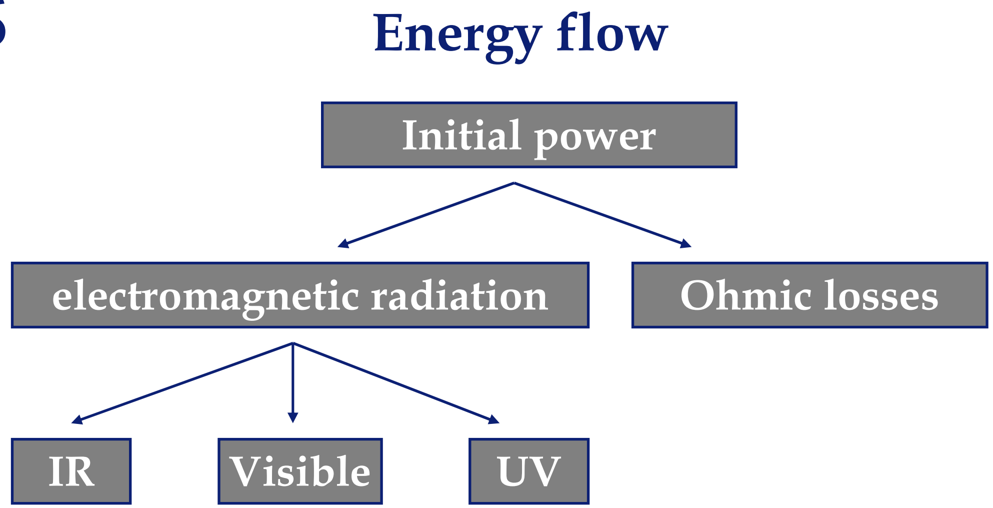
Colour Rendering Index (CRI)

- Measures color reproduction of light sources with respect to test colors
- Measurement:
- Reflection of 8 or 14 test panels are compared under light source versus incandescent illumination
- Scale $0 \leq \text{CRI} \leq 100$
- CRI = 0 monochromatic source
- CRI = 100 broadband source



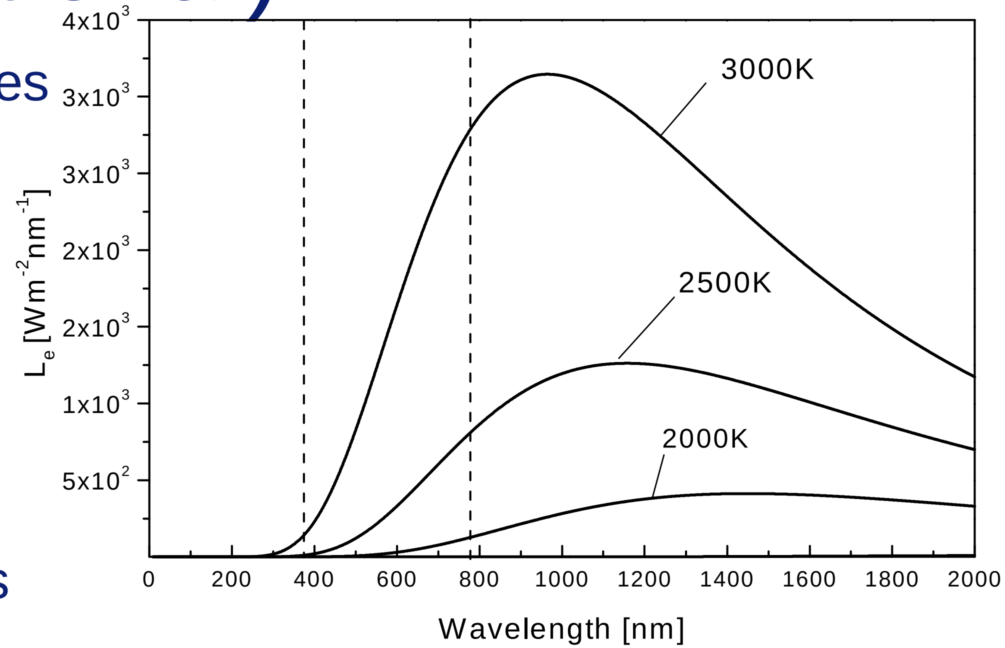
Incandescent light sources





- Principle
- Ohmic heating of filament by electric current. Power consumption: $P = U^2/R$
- Light-emission in thermial equilibrium. Planck‘s law: $L_e = (c_1/\lambda^5)*1/(\exp(c_2/\lambda T)-1) *10^{-9}$ [W/m²nm]

Light bulbs (conventional)



- Visible light fraction increases with increasing filament temperature

- Problem
- Tungsten evaporates from filament
- Resistivity R increases
- Filament temperature keeps increasing until it burns

- Gas filling
- Argon, Krypton or Nitrogen reduce Tungsten-evaporation and increase lifetime

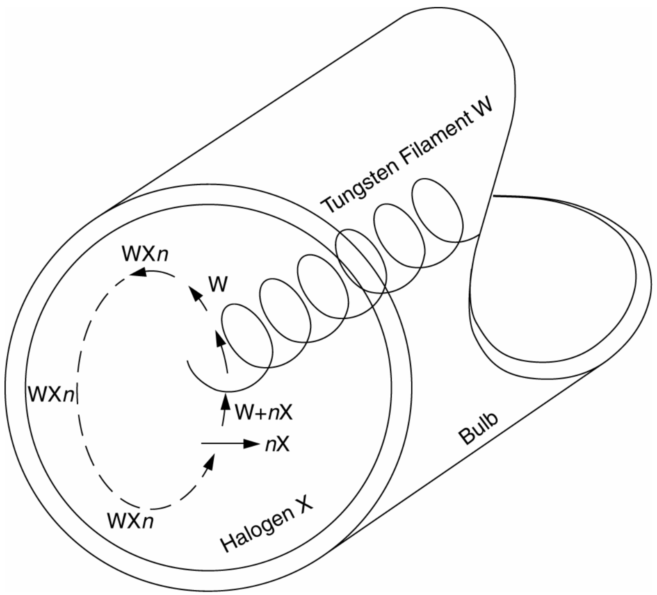
Lifetime strongly depends on temperature

2800 K	1000 h
3200 K	100 h
3400 K	5 h

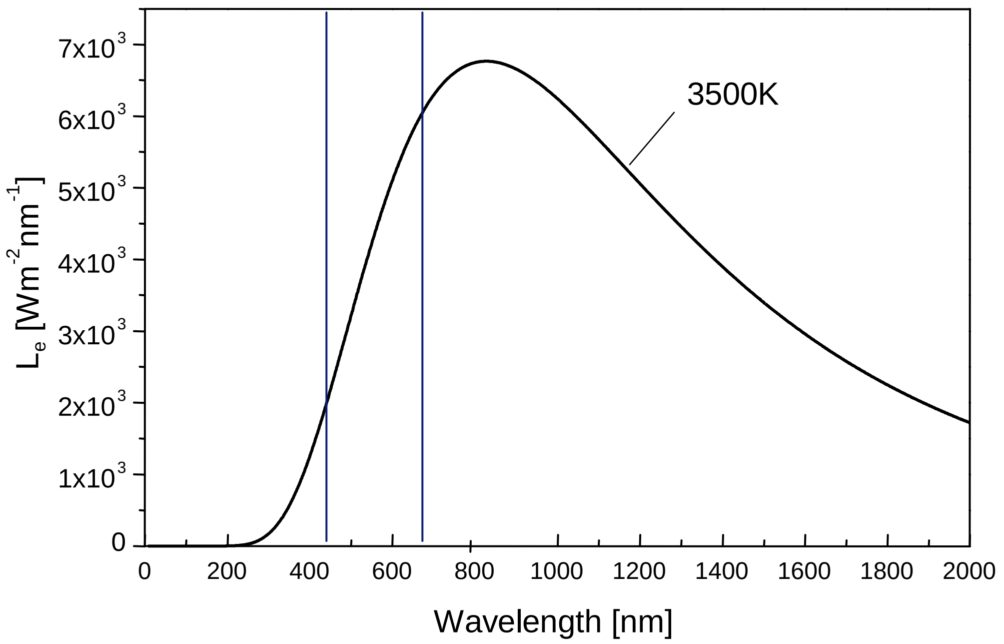
Halogen lamps

- Filling: I_2, CH_3Br or HBr
- Higher energy efficiency through higher burning temperature
- Shift of emission spectrum increases UV fraction

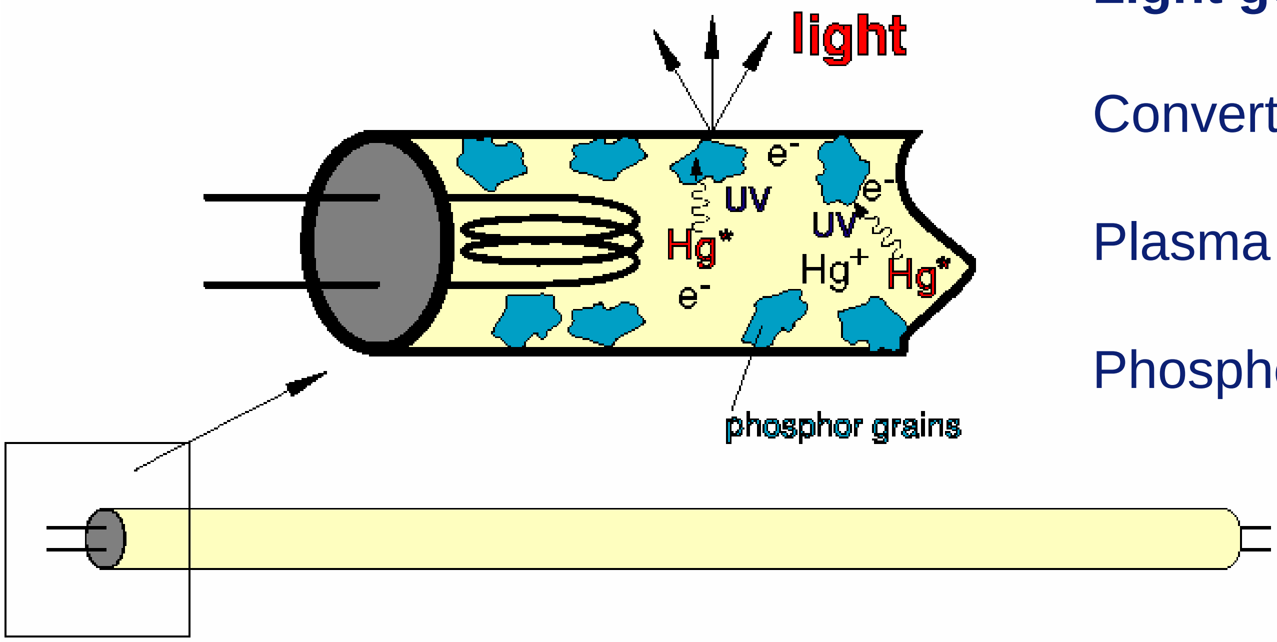
Tungsten-Halogen cycle



Emission spectrum



Hg- low pressure lamp (fluorescent tube)



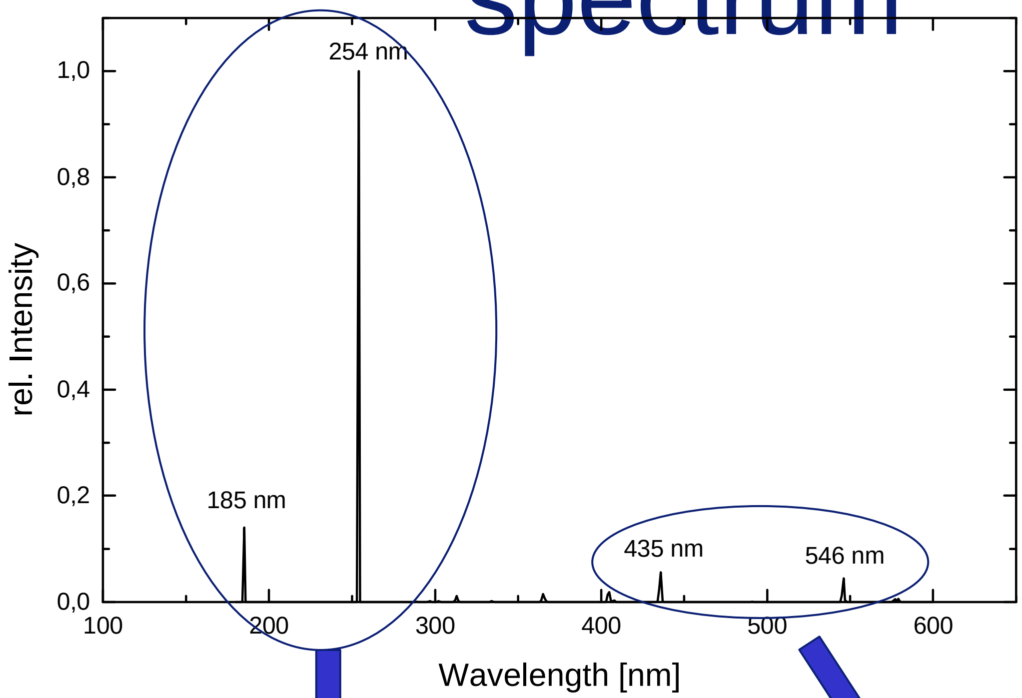
Light generation principle

Converter → electrical power

Plasma → UV-radiation

Phosphor → visible light

Hg-Plasma spectrum



Plasma lines at

185 nm (12 %)

254 nm (85 %)

405, 435, 546, 577 nm (3%)

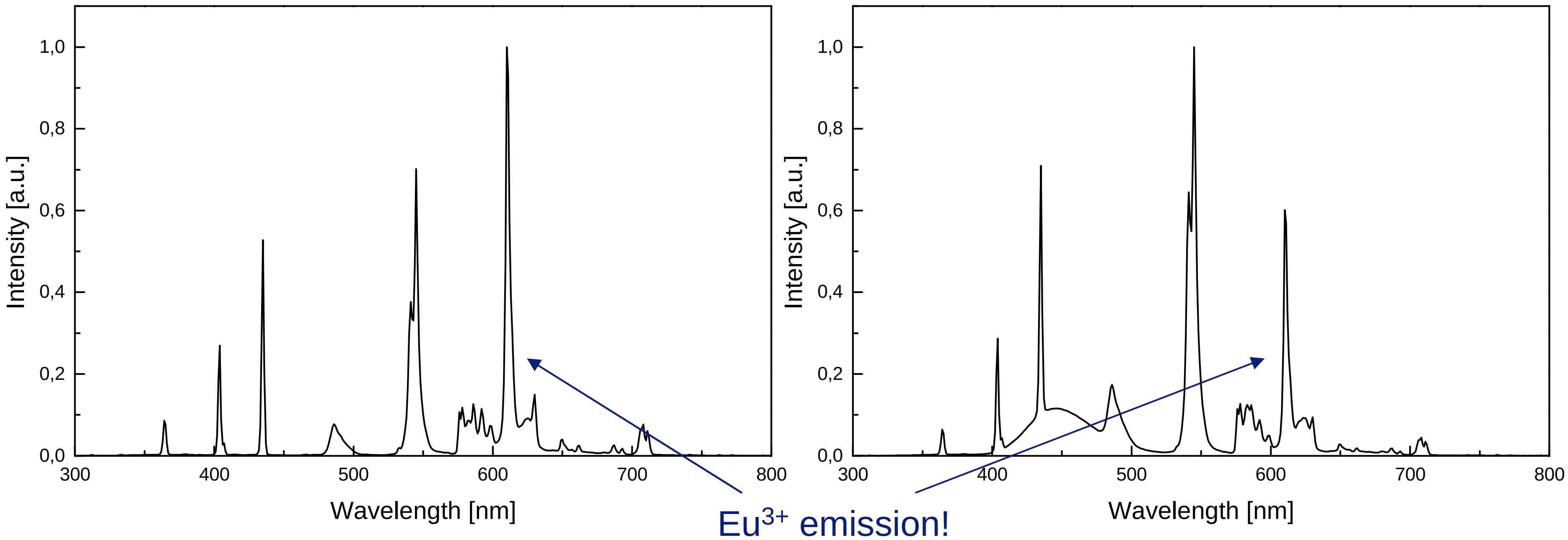
Conversion of UV part (quantum deficit)

Blue light remains in visible spectrum

Typical spectra of fluorescent tubes

2700 K Lampe mit CAT and YOX

6500 K Lampe mit BAM, CAT und YOX



Two converter and three converter mixture.

Efficiency of fluorescent tubes

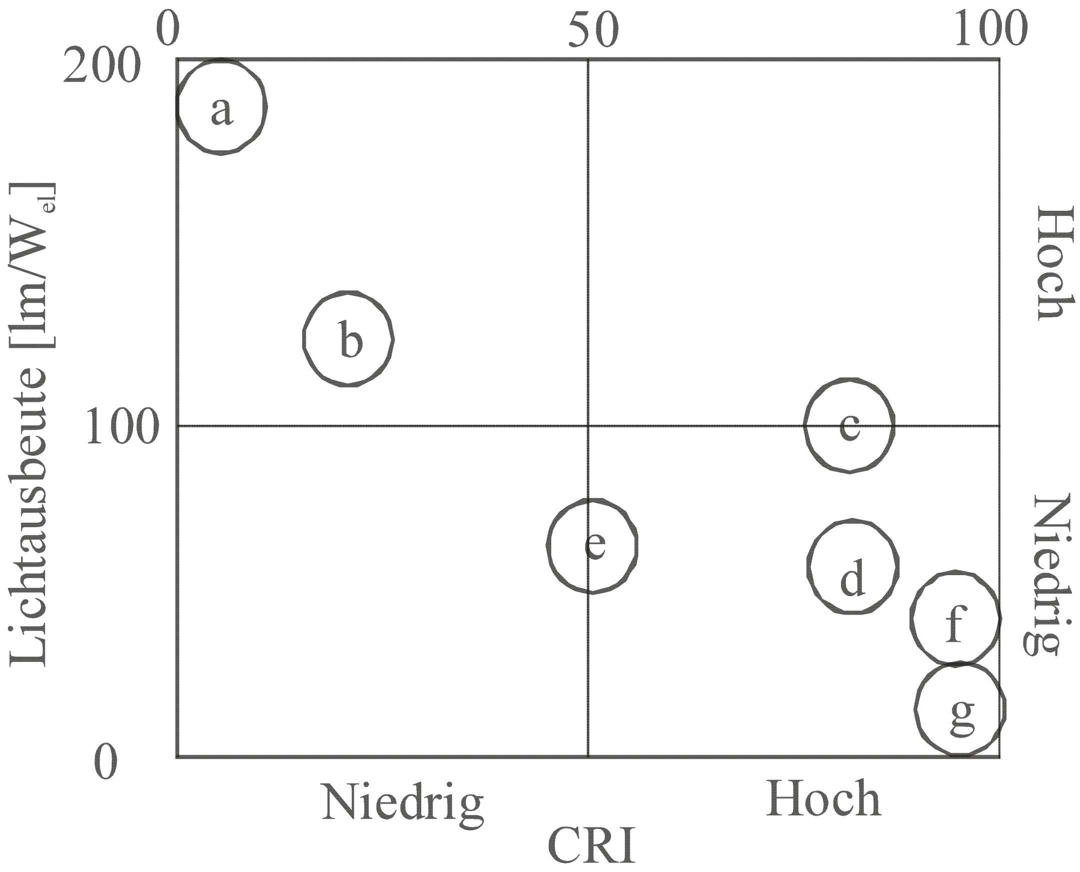
$$\varepsilon = \varepsilon_{dis} * QD*QA$$

- ε_{dis} = Plasma efficiency
- Quantum-deficit = $[\lambda_{Plasma}/\lambda_{converter}]$ = 0.46
- Quantum-efficiency = $N_{emit.\ photons}/N_{abs.\ photons}$ ~ 0.9

Fluorescent tubes ε_{dis} = 70 % $\Rightarrow$ **ε = 29 % (100 lm/W)**

Energy saving lamps ε_{dis} = 40 % $\Rightarrow$ **ε = 16 % (55 lm/W)**

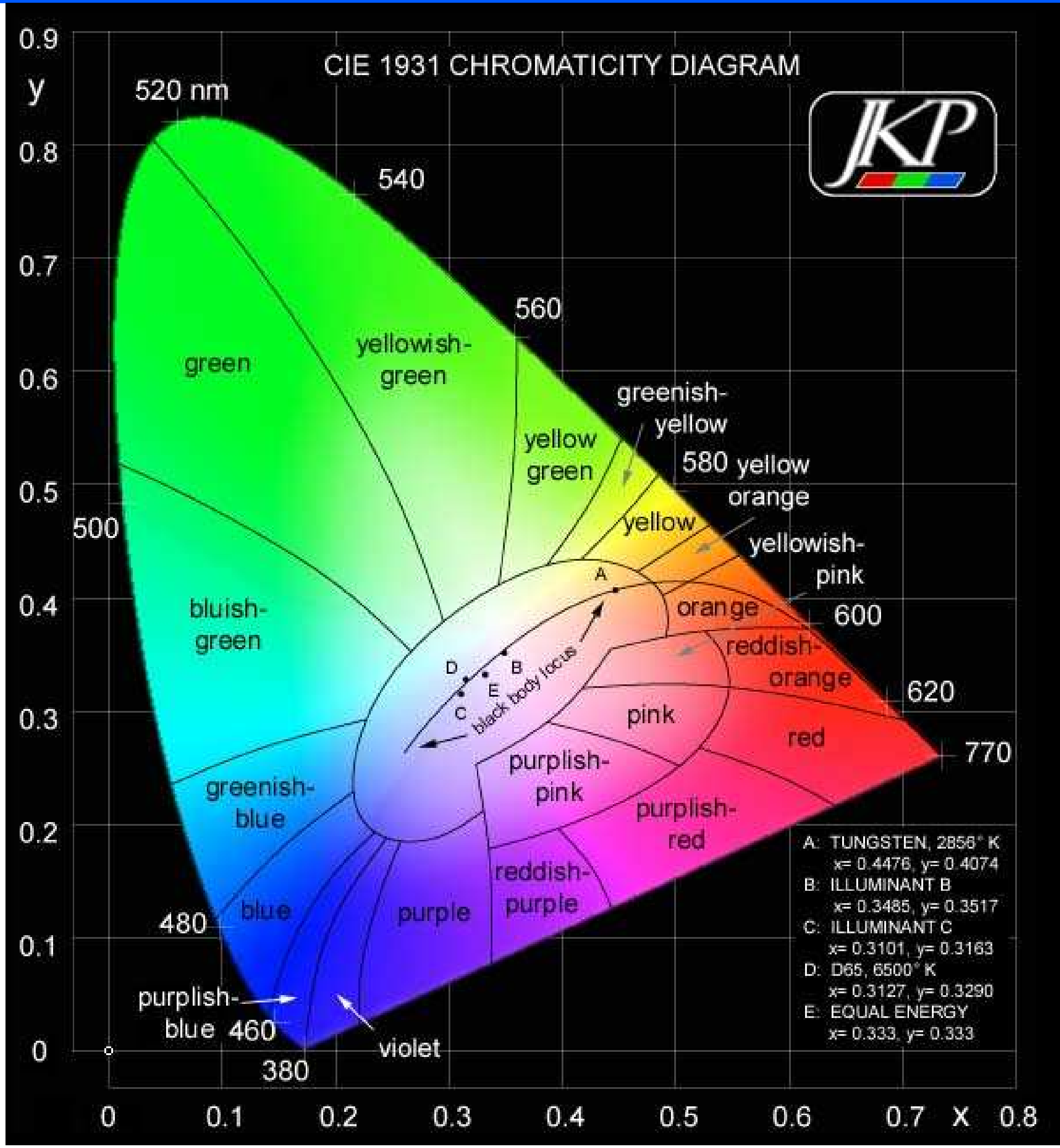
Comparison of light sources



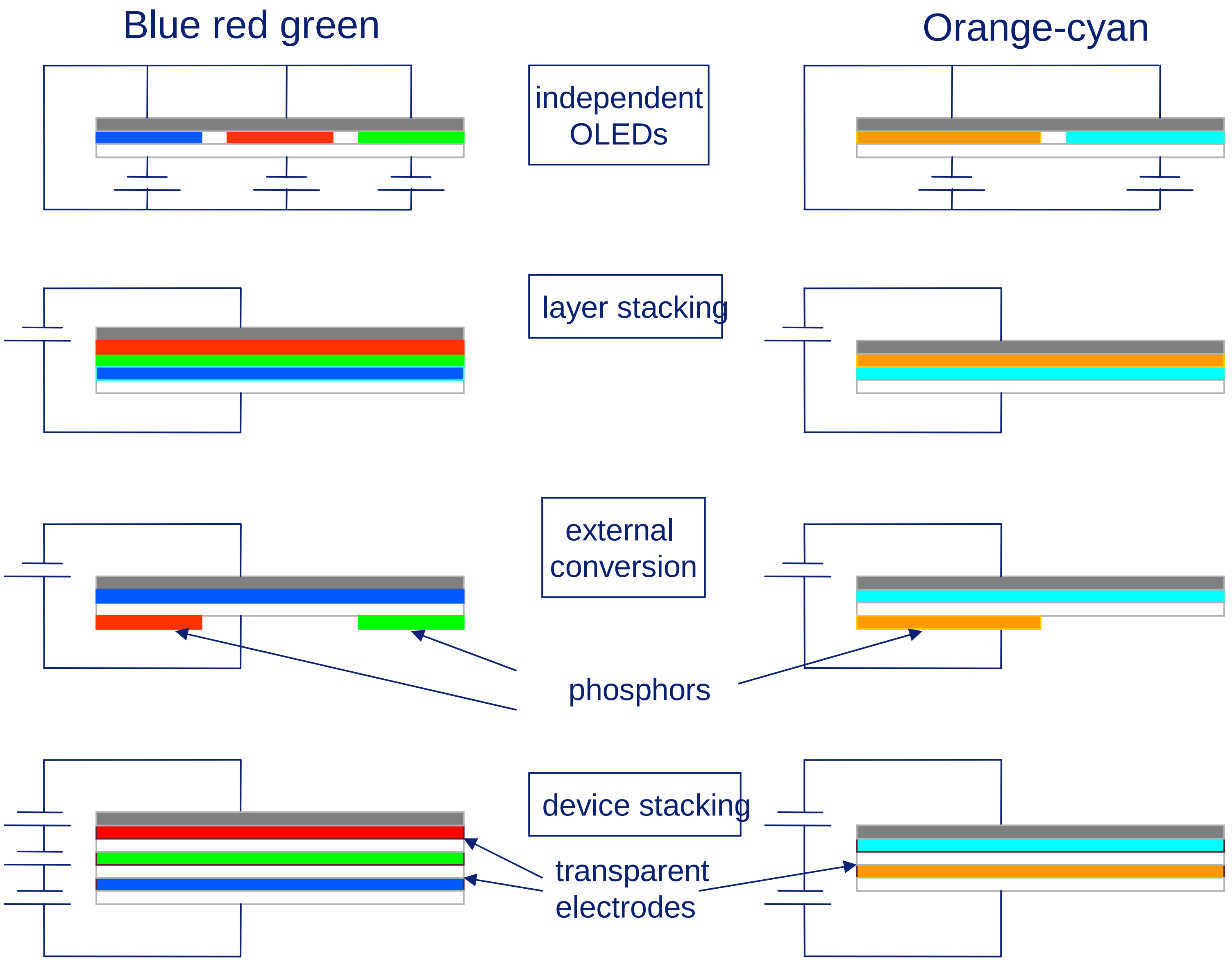
- a Na-low pressure
- b Na-high pressure
- c fluorescent tube
- d energy saving bulb
- e Hg-high pressure
- f Halogen
- g Light bulb

White light generation I

- White combinations
  - Warm white
  - Cold white

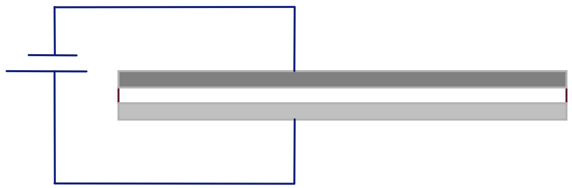


White light generation II



White light generation III

In principal, of course:
Intrinsic white

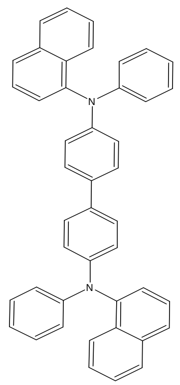


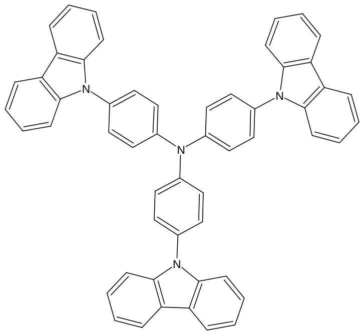
How to make OLEDs I

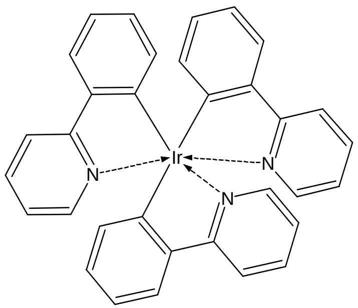
- Vacuum evaporation
- Organic vapour phase deposition (OVPD)

Evaporable small molecules:

- Molecular weight < 1000
- No linear repetition of simple building block







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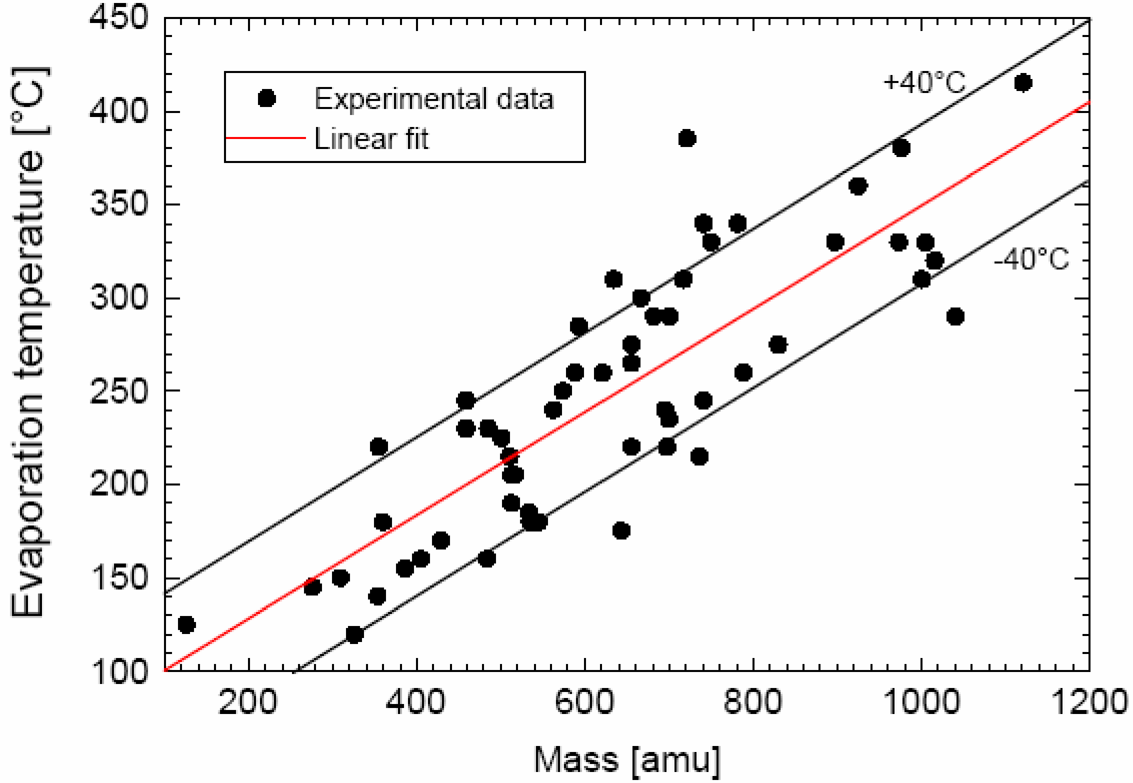
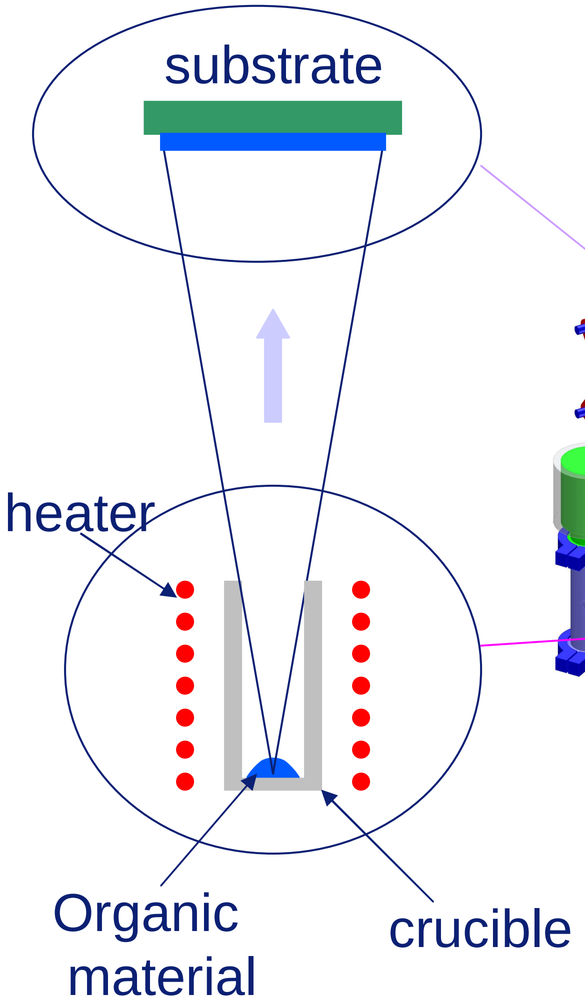
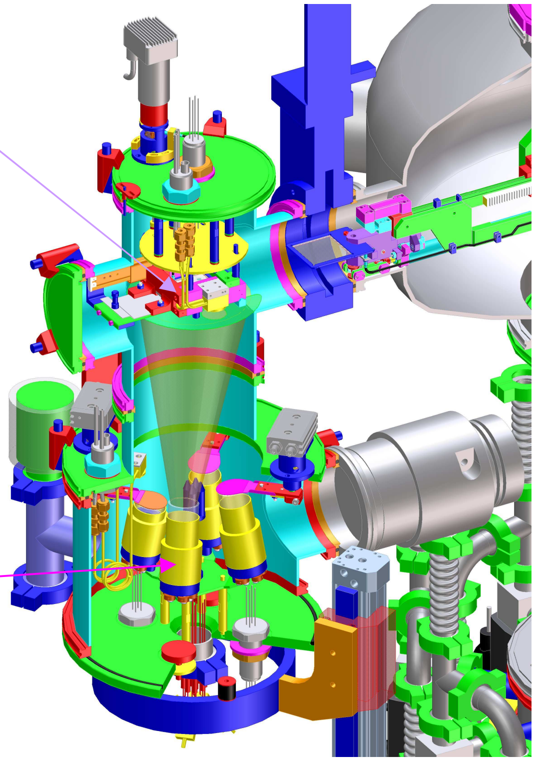
How to make OLEDs II



Octopus: vacuum evaporation



Point sources

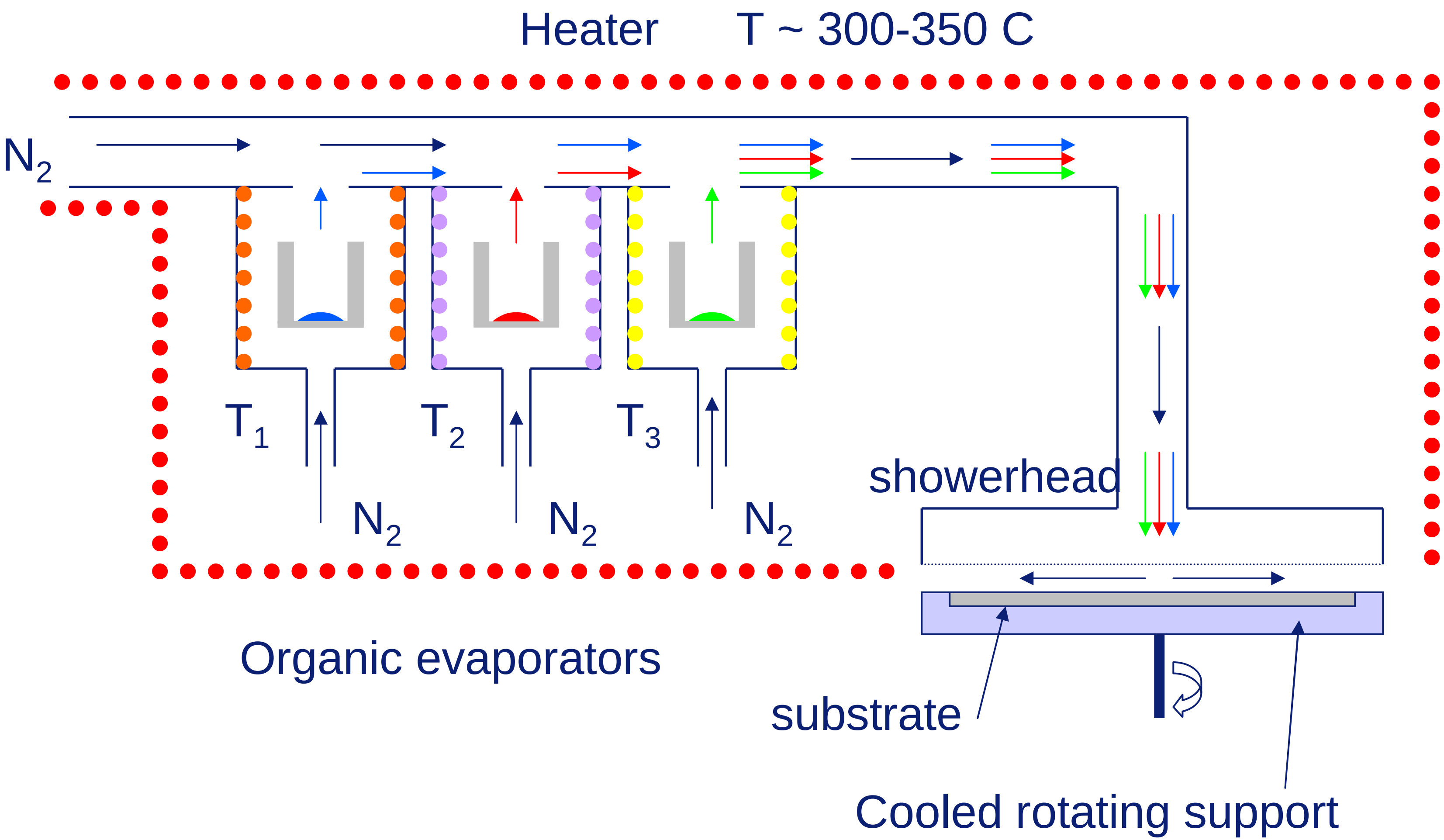


Octopus

$T_{crucible} \sim 150 – 400$ C

OVPD

organic vapour phase deposition, AIXTRON

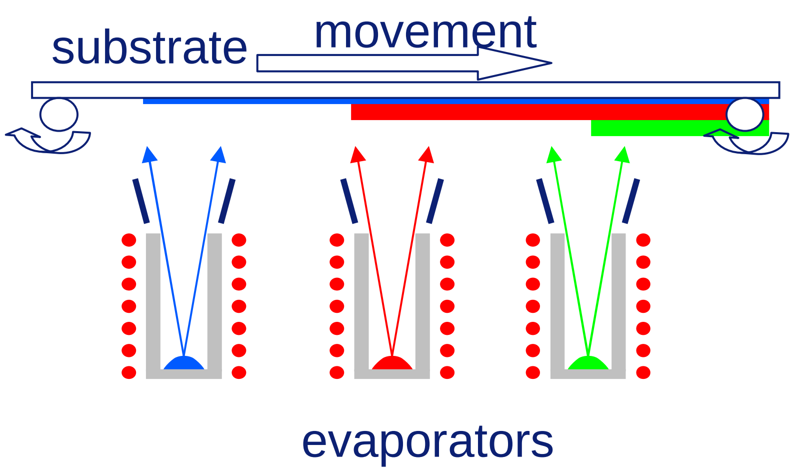


OVPD

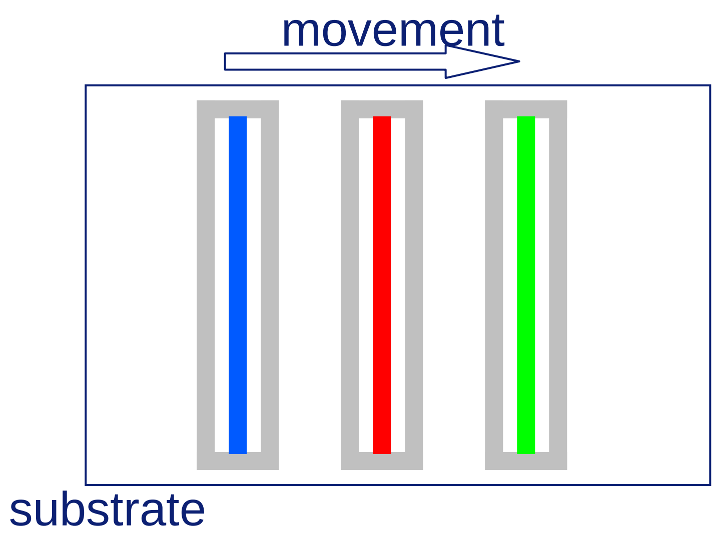
organic vapour phase deposition, AIXTRON

PHILIPS Linear sources for evaporation or OCVD

- higher throughput
- Larger substrate size
- Better substrate coverage
- requires sophisticated thickness control
- large amount of material needed
- Under test and construction at several places (e.g. Applied Films)



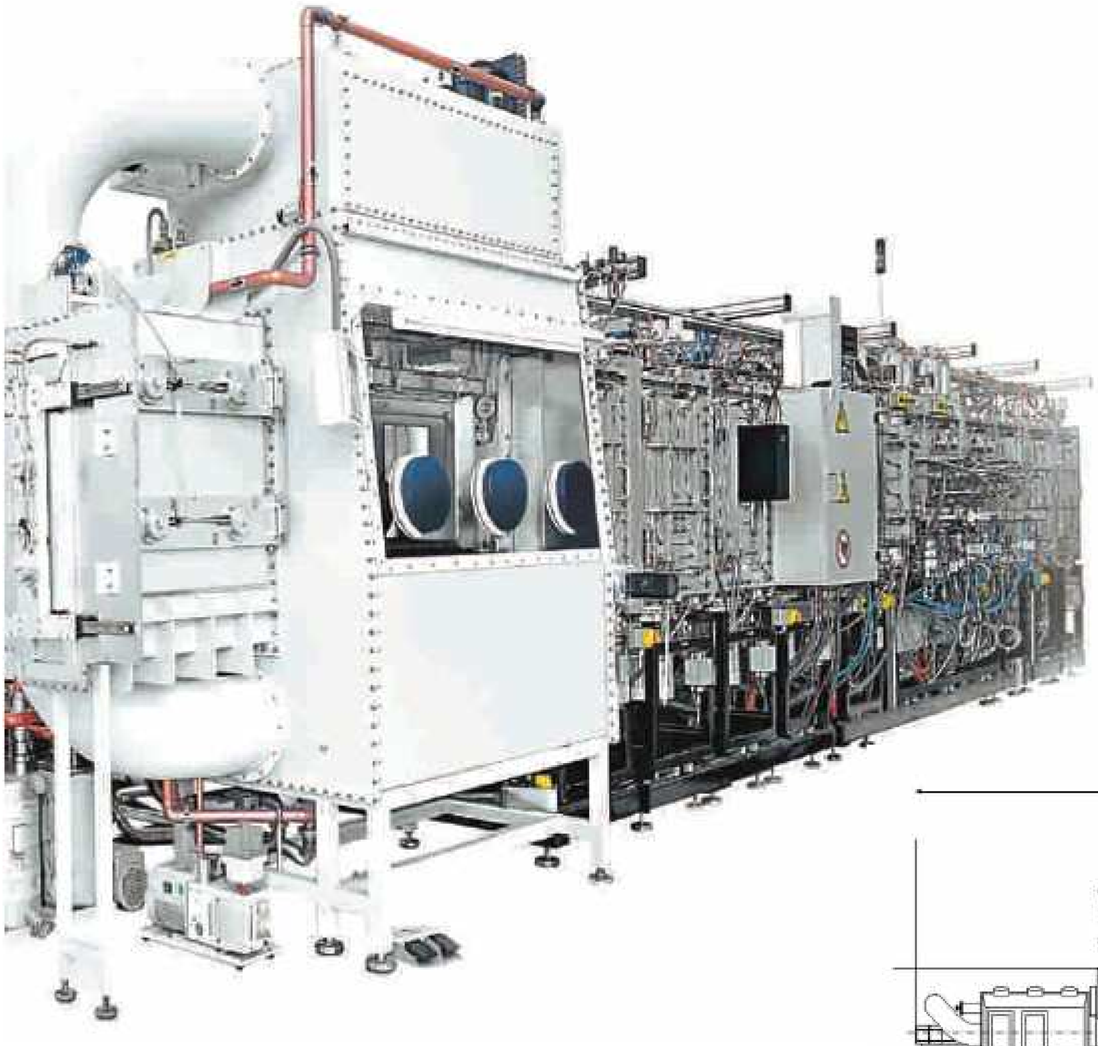
From the side



From above

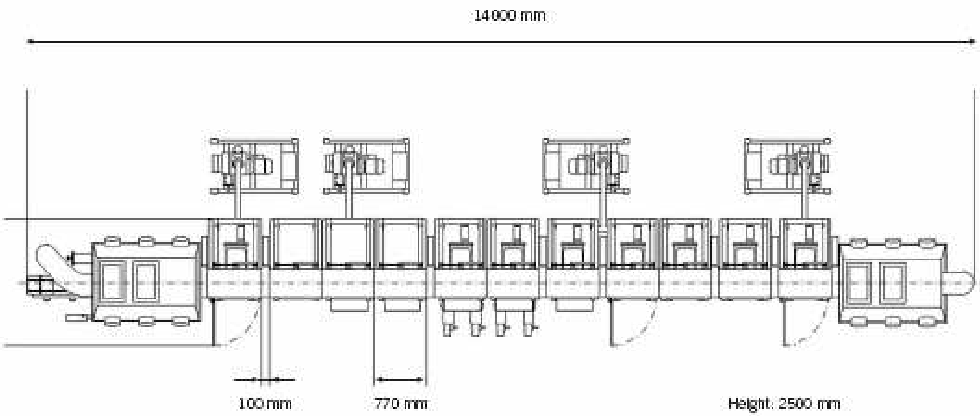
PHILIPS Linear sources for evaporation

Applied Films



Technical Data

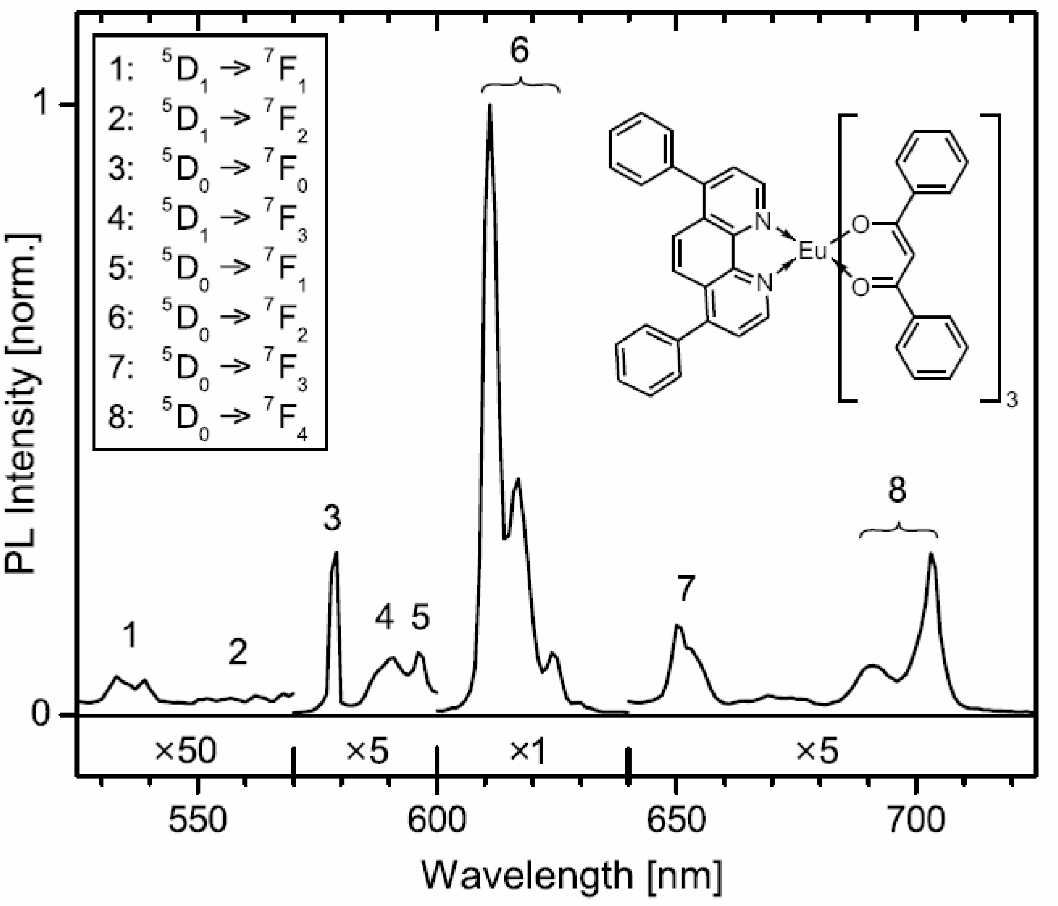
Maximum coating window	up to 400 x 500 mm
Vertical coating length	up to 500 mm
Ultimate pressure	≤ 5 x 10^{-8} hPa



- Eu^{3+}: red emission (612 nm); very interesting
- Tb^{3+}: green emission; nice, but many other choices in terms of Ir-complexes
- Sm^{3+}, Dy^{3+},Ho^{3+},Nd^{3+}… not really efficient enough for us
- Gd^{3+}: is a special case

Eu^{3+} emission

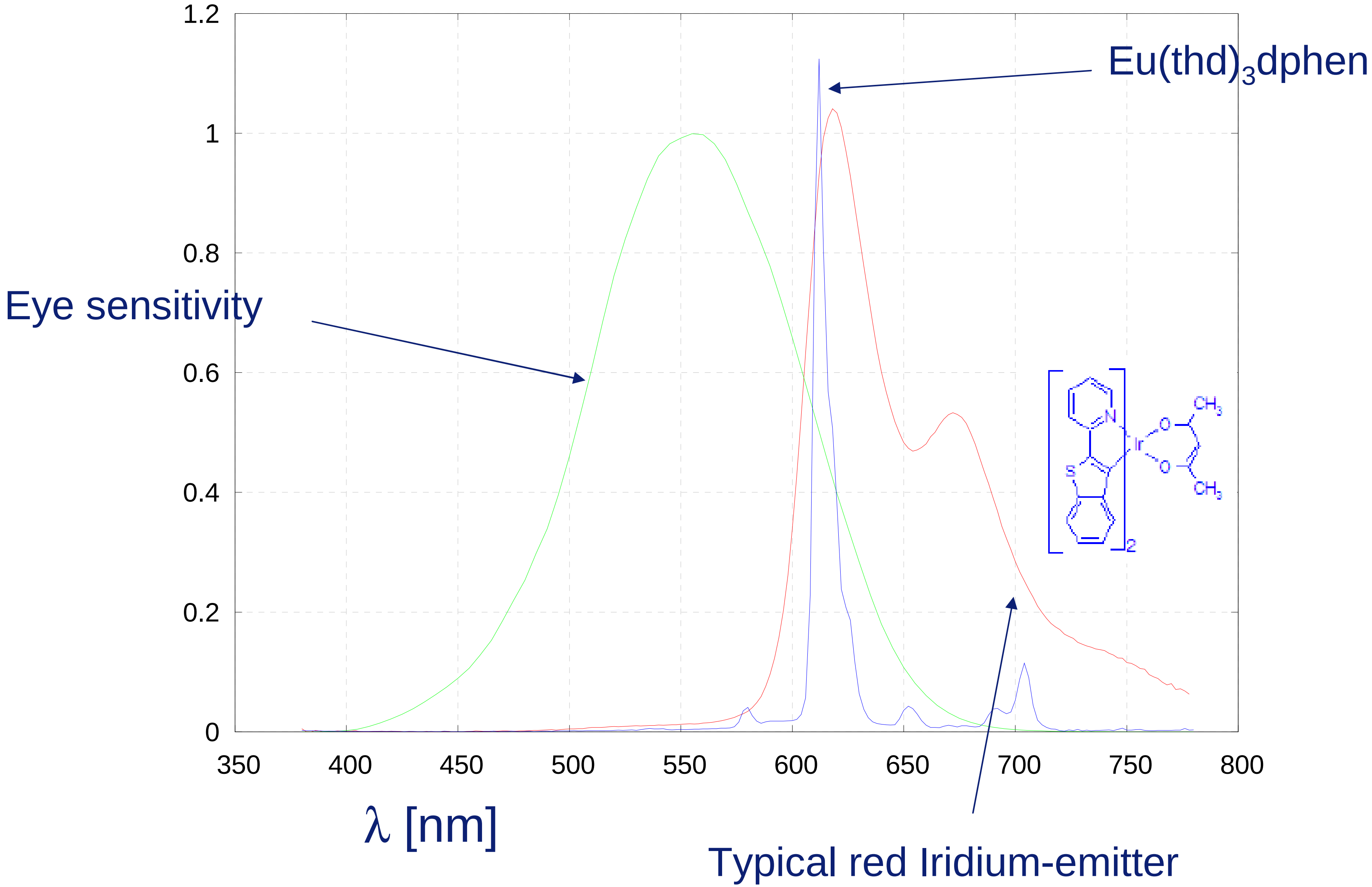
- Intra-atomic transitions in the 4f-shell
- Shielded by 5*s*5*p* electrons



Exciton quenching in highly efficient europium-complex based OLEDs

T.W. Canzler and J. Kido

PHILIPS Problems with red emitters



Efficiencies of Eu-complexes

Substance	PL quantum efficiency [%]	decay [msec]
Eu $(thd)_3$ dpphen	26	0.72
Eu $(thd)_3$ phen	9	0.80
Eu $(ttfa)_3$	9	0.13
Eu $(ttfa)_3$phen	72	0.77
Eu $(ttfa)_3$ dpphen	47	0.58
Eu $(ttfa)_3$ Clphen	75	0.79
Eu $(fod)_3$ phen	30	0.83
Eu $(fod)_3$ dpphen	48	0.86
Eu $(tfnb)_3$ phen	56	0.45
Eu $(tfnb)_3$ dpphen	64	0.61
Eu $(dbm)_3$ phen	15	0.39
Eu $(dbm)_3$ dpphen	25	0.35

Measured as solid (powder) in standard setup for inorganic lamp phosphors

!!!

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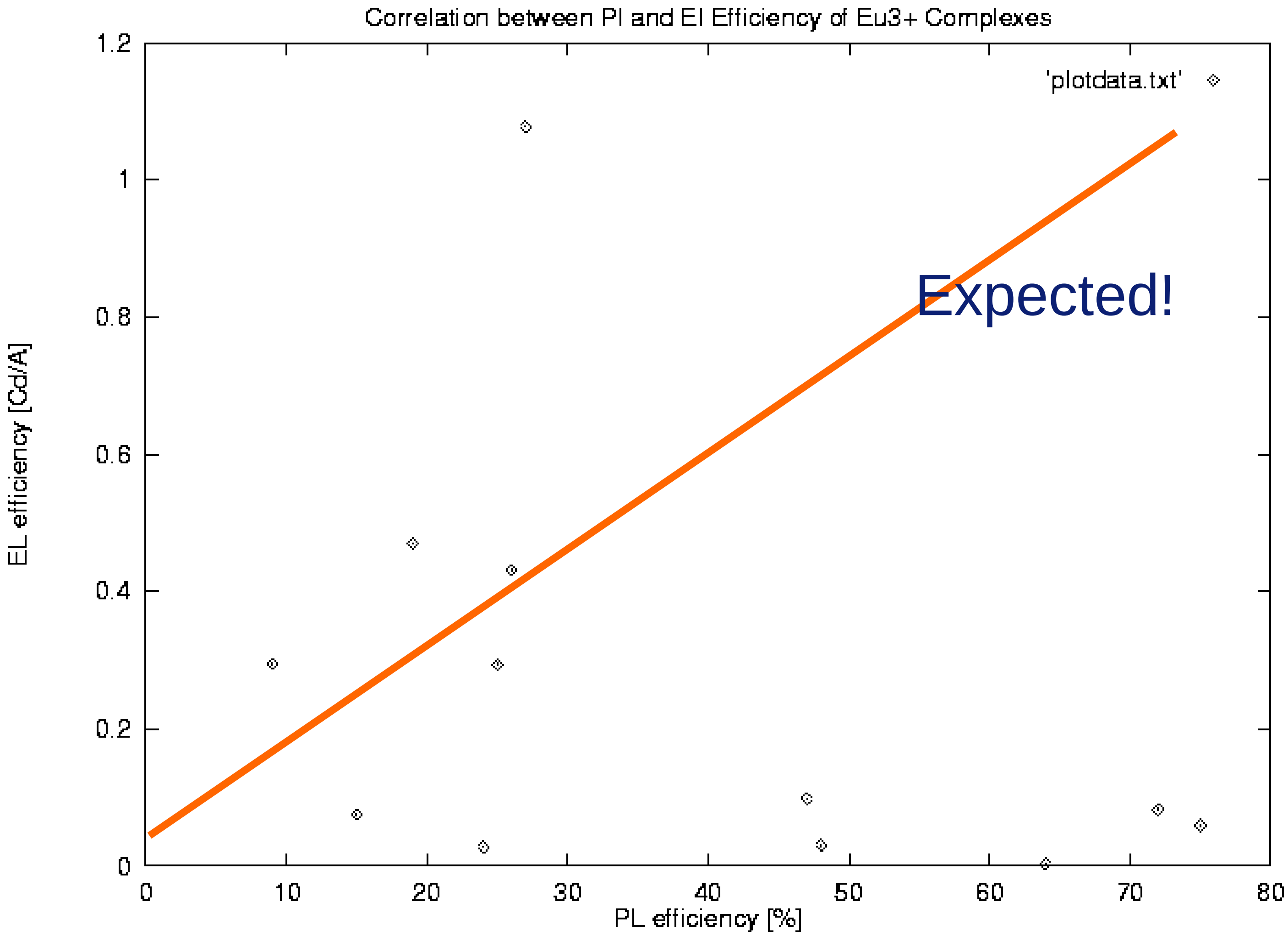
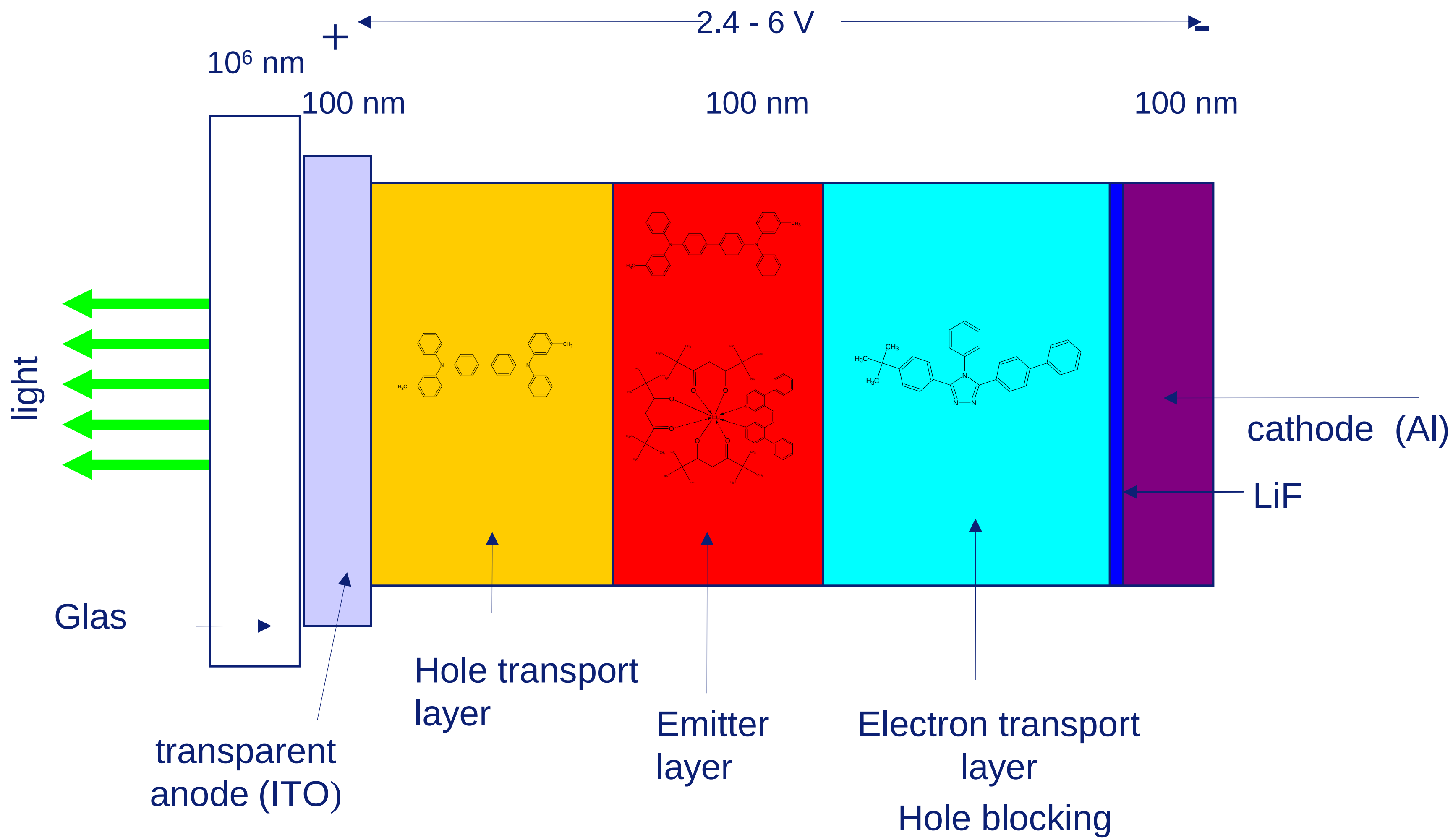
Efficiencies of Eu-complexes in EL



Warning: “old” data, new experiments may show different results!

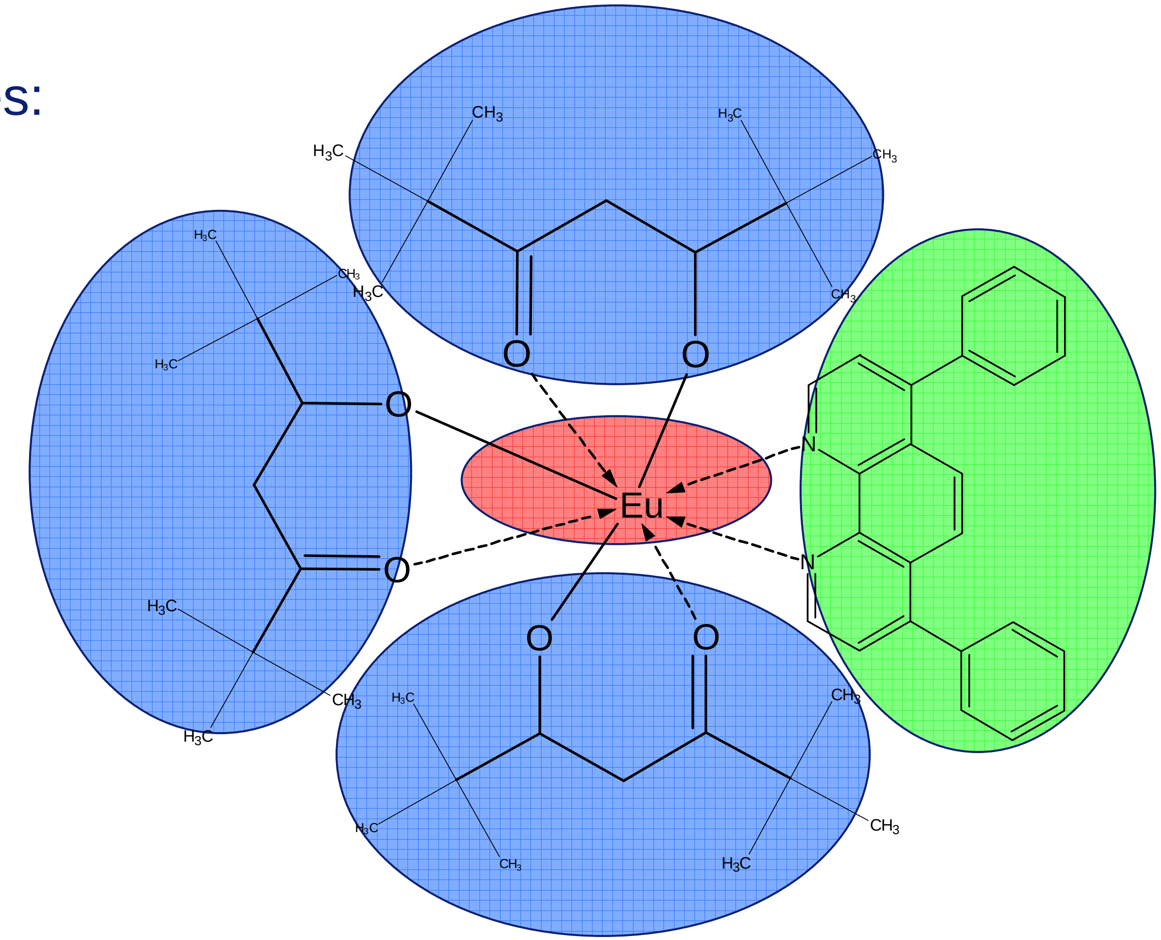
Typical OLED with Eu-complex



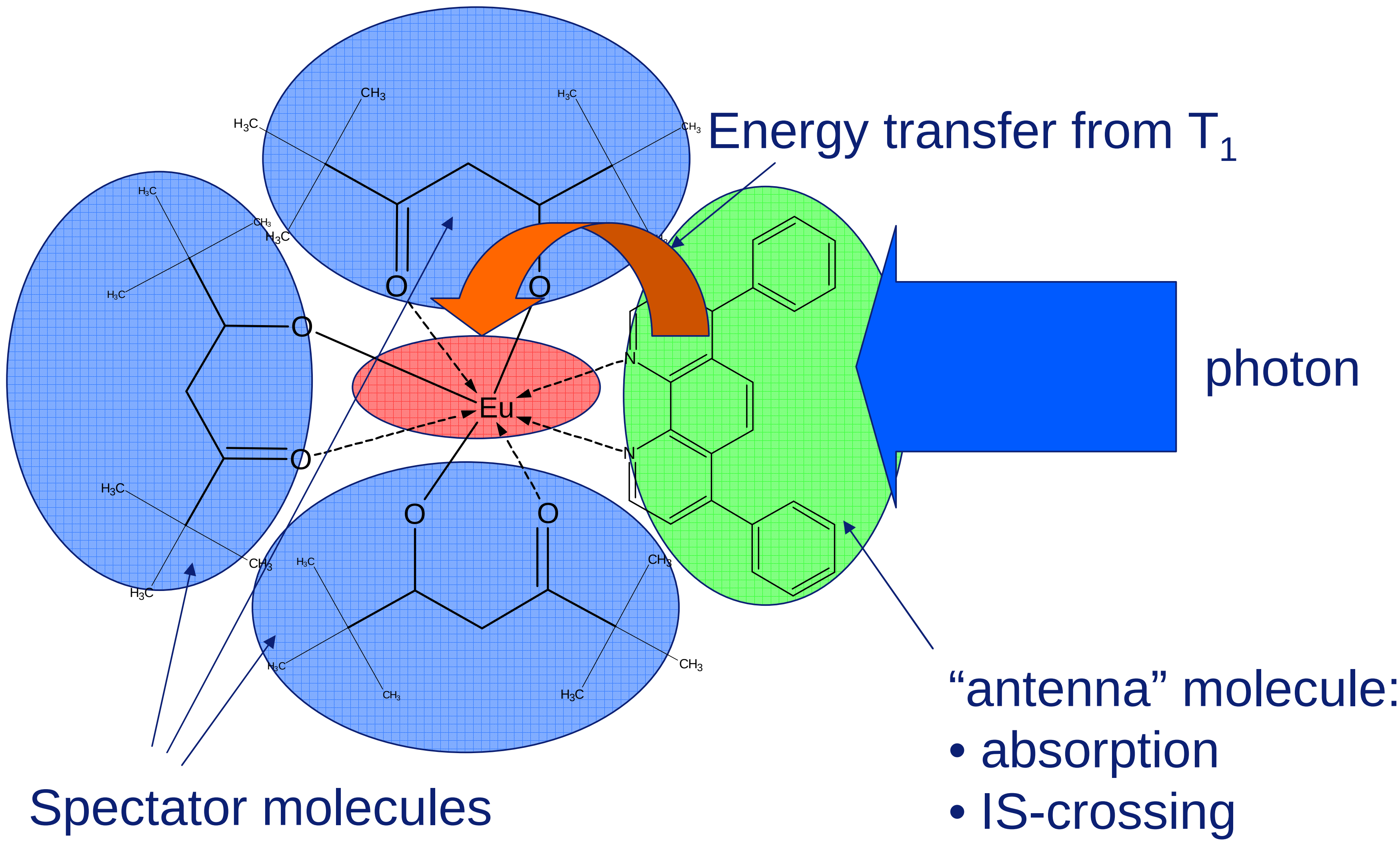
Eu^{3+} emitters

- 5 loosely coupled entities:
- Three charged ligands
- The uncharged ligand
- The rare-earth ion

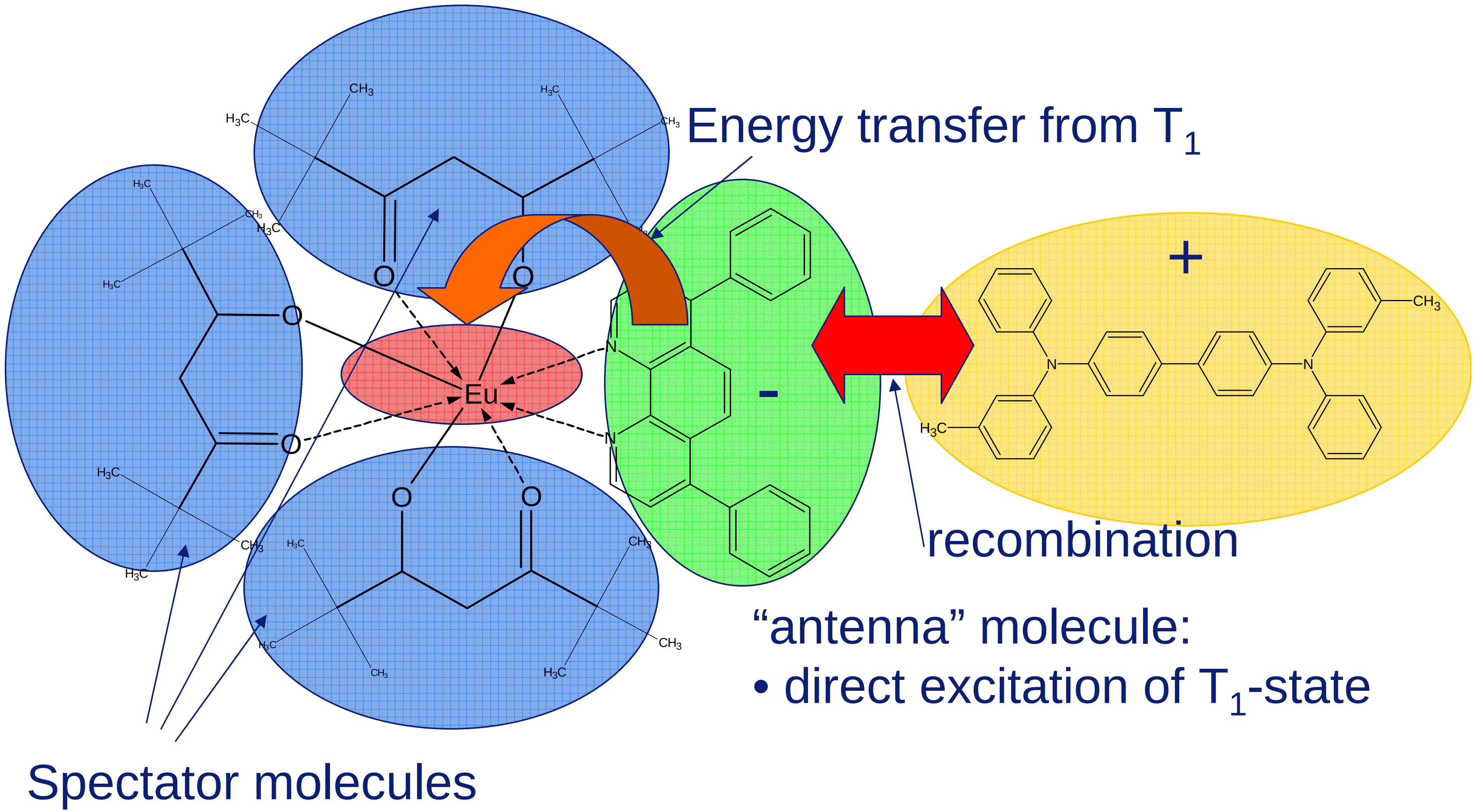
- Offers possibility to tune the properties of the complex: charge transport or exciton transport
- Example: only bphen participates in charge transport



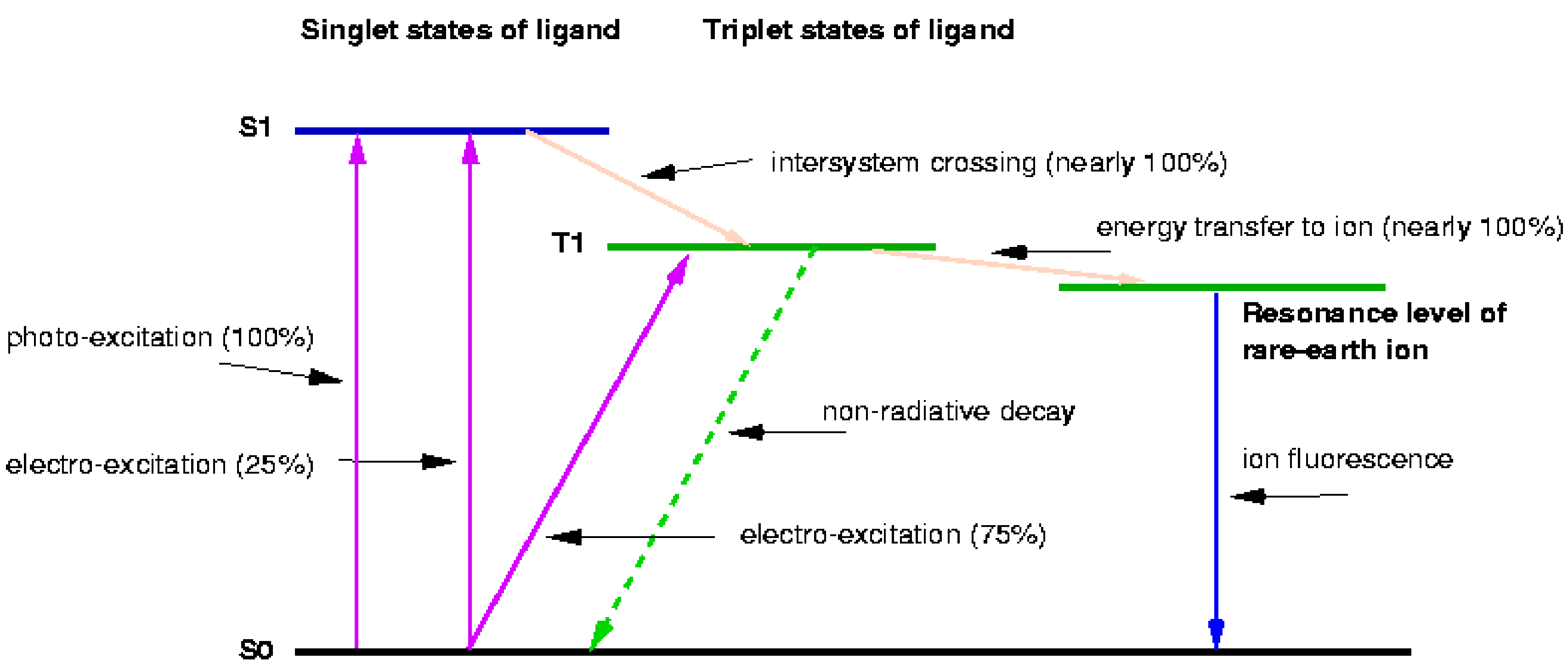
PHILIPS Eu^{3+} emitters: photoexcitation



Eu^{3+} emitters: electroexcitation



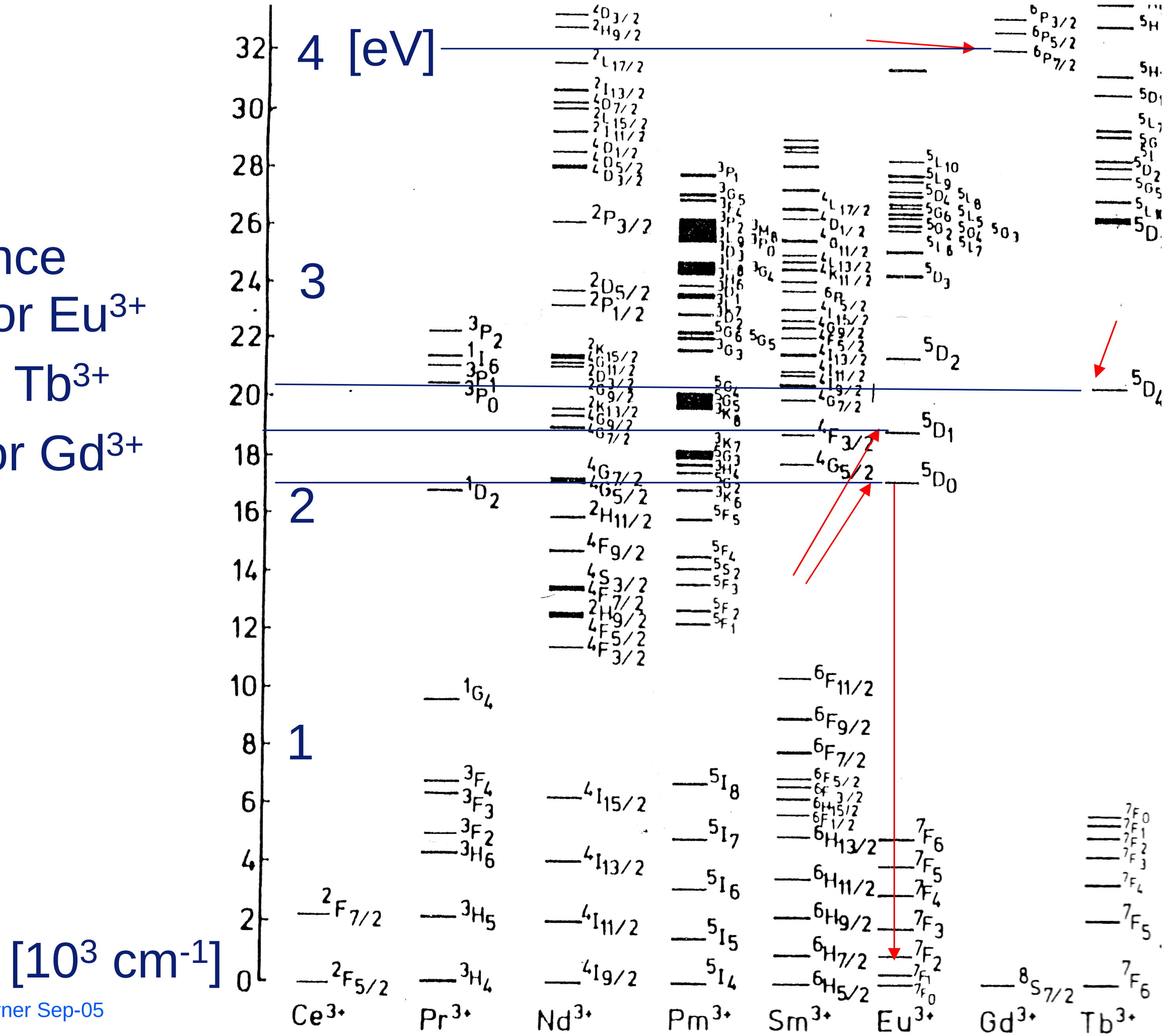
Eu^{3+} emitters



Energy transfer chain in rare-earth complexes under photo- and electro-excitation

RE^{3+} energy levels

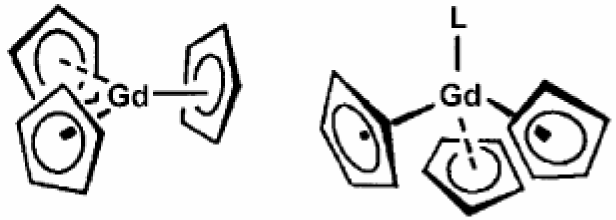
- Two resonance levels for Eu^{3+}
- One for Tb^{3+}
- None for Gd^{3+}



Gd^{3+} emitter: a special case

- Gd3+ has high-lying state, normally no energy transfer from ligand to ion
- Redox-inert
- Paramagnetic
- Induces S-T mixing: radiation due to ligand phosphorescence
- Radiative lifetime of $GdCp_3$: 2.3 µsec
- Unfortunately air sensitive

- Gd is much cheaper than Ir
- less problems with patents
- Greater risks: need stable complexes with high QE, short radiative lifetime and good emission spectrum



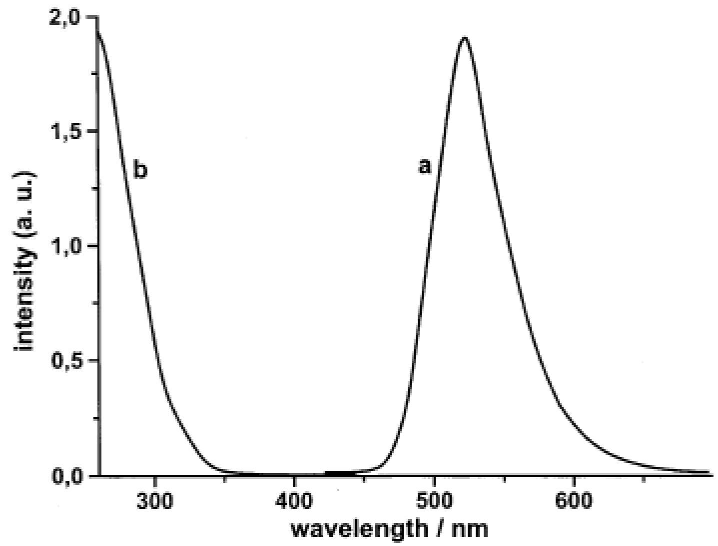


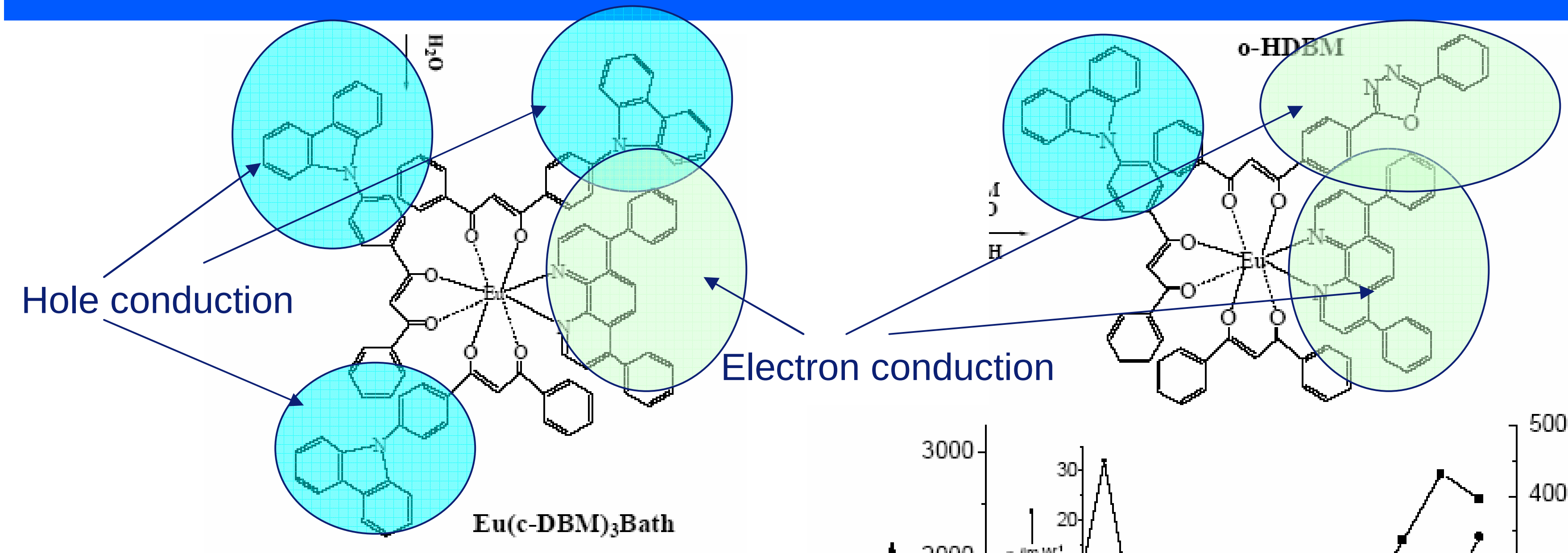
Fig. 1. Electronic emission (a) and excitation (b) spectrum of $GdCp_3$ in dry diethylether at 298 K, $\lambda_{exc} = 250$ nm, $\lambda_{em} = 500$ nm.

A. Strasser, A. Vogler / Chemical Physics Letters 379 (2003) 287–290

Eu^{3+} complexes: requirements

- Evaporability
  - Need uncharged complexes for evaporability: 3 charged ligands
  - Coordinative saturation needed for evaporability:1 uncharged ligand
  - Thermal stability (co-ligand!!)
- Charge transport capabilities of ligands
  - For holes: triarylamines, carbazoles
  - For electrons: phenathrolines
  - Ambipolar: aromatic molecules, fluorene, napthalene, …
- Energy transfer from ligand to Eu-ion
  - T_1 of ligand larger than resonance level: Eu^{3+} with $^5D_0$at 17270 cm^{-1} and $^5D_1$ at 19030 cm^{-1}

Eu^{3+} complexes: requirements



ITO

(TPD) (30 nm)

Eu(DBM)2(cDBM)Bath:PBD (1:1, molar ratio)(40 nm)

PBD (30 nm)

MgAg

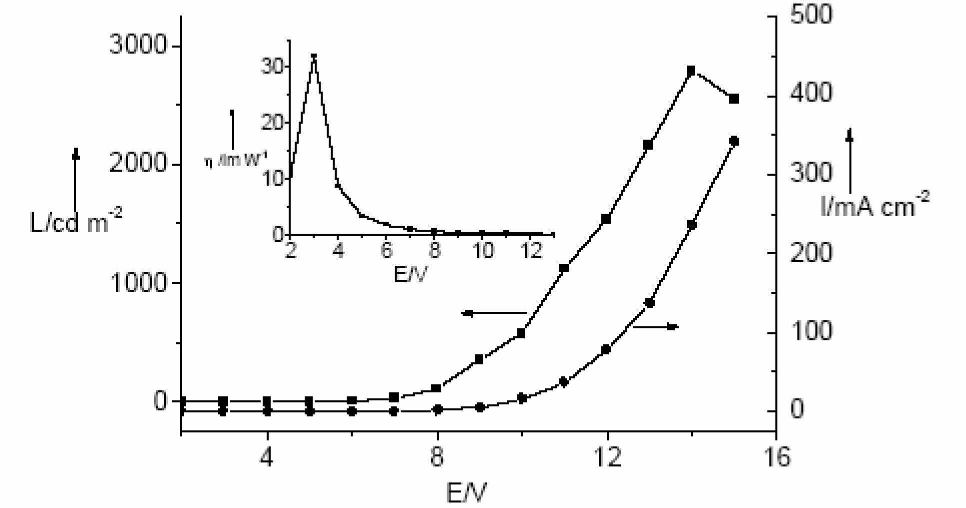


Fig. 2 The luminance-voltage and current-voltage characteristics of device 6. Inset: The EL efficiency-voltage characteristic of device 5.

Pure red electroluminescence based on a functionalized EuIII complex**

ZuQiang Bian, Min Guan, YanYi Huang,FuYou Li, Hao Xin, ChunHui Huang*
(Advanced Materials??)

- Fluorescent states: 10^{-10} to 10^{-7} sec
- Phosphorescent states: 10^{-6} to 10^{-4} for transition metal complexes
- Phosphorescent states in general: up to several sec. at 77K
- Eu^{3+} , Tb^{3+} complexes: 10^{-4} to 10^{-3} sec
- Gd^{3+} complexes: 10^{-6} to 10^{-1} sec

- The longer the lifetime, the more quenching!

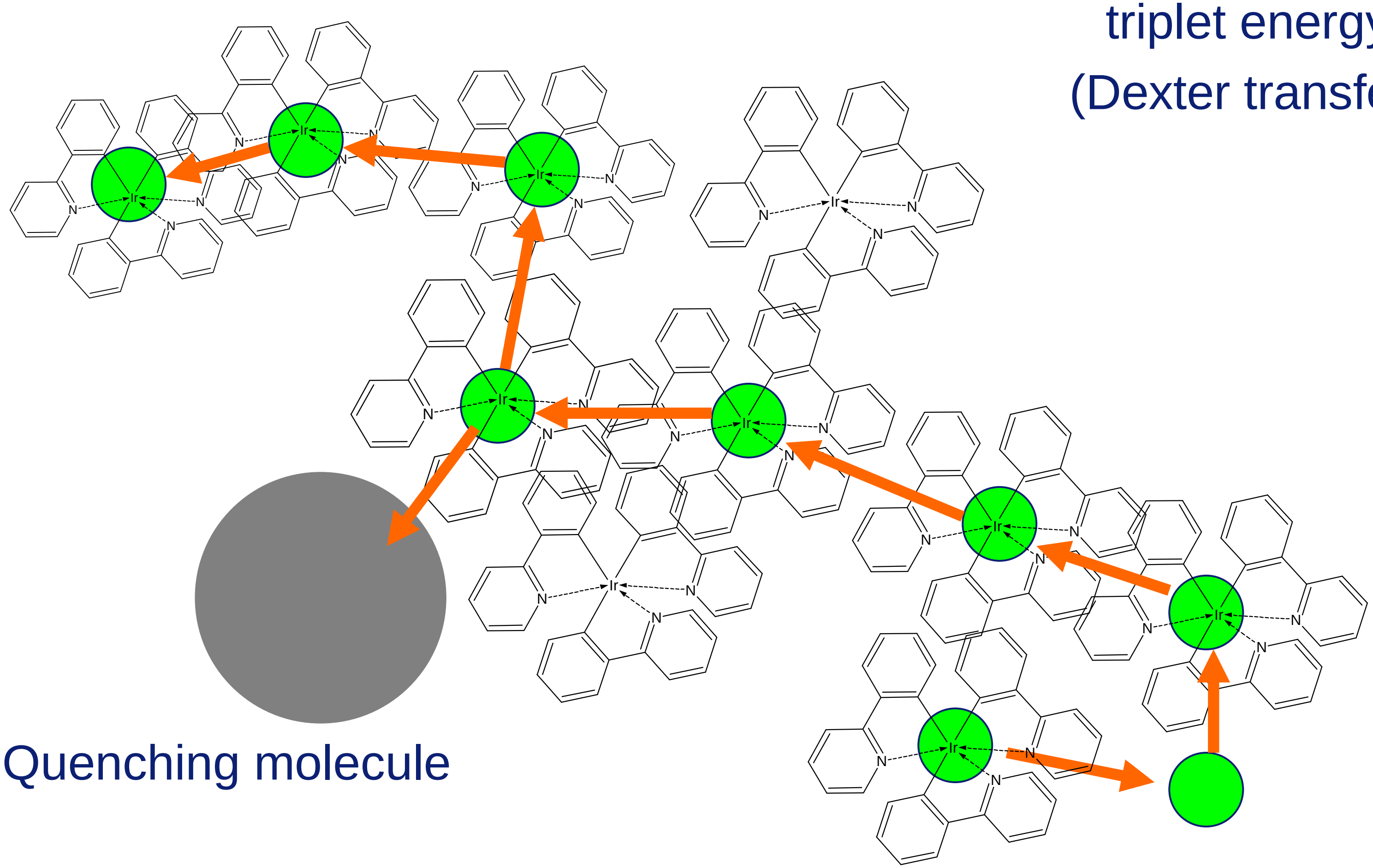
Problems of electroexcitation

- Long radiative lifetime of excited state compared to fluorescent emitters
- Quenching by charge carriers

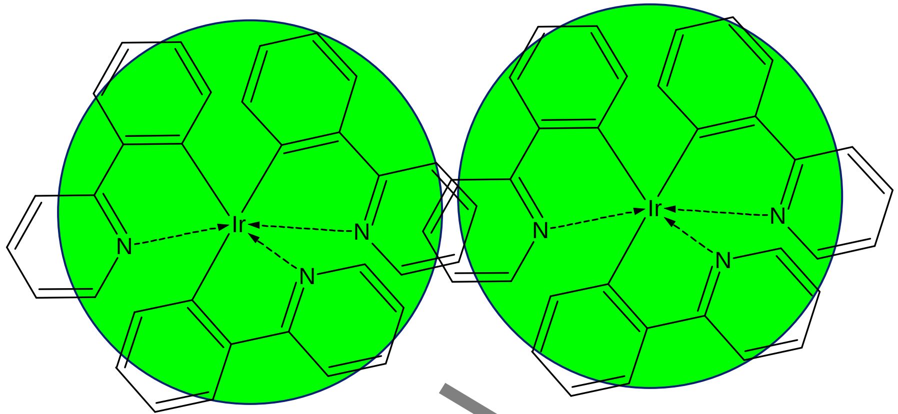
- Energy transfer to matrix: mobile triplets
- Triplet-triplet annilihation

OLED structure optimisation : quenching I

Transfer of triplet energy (Dexter transfer)

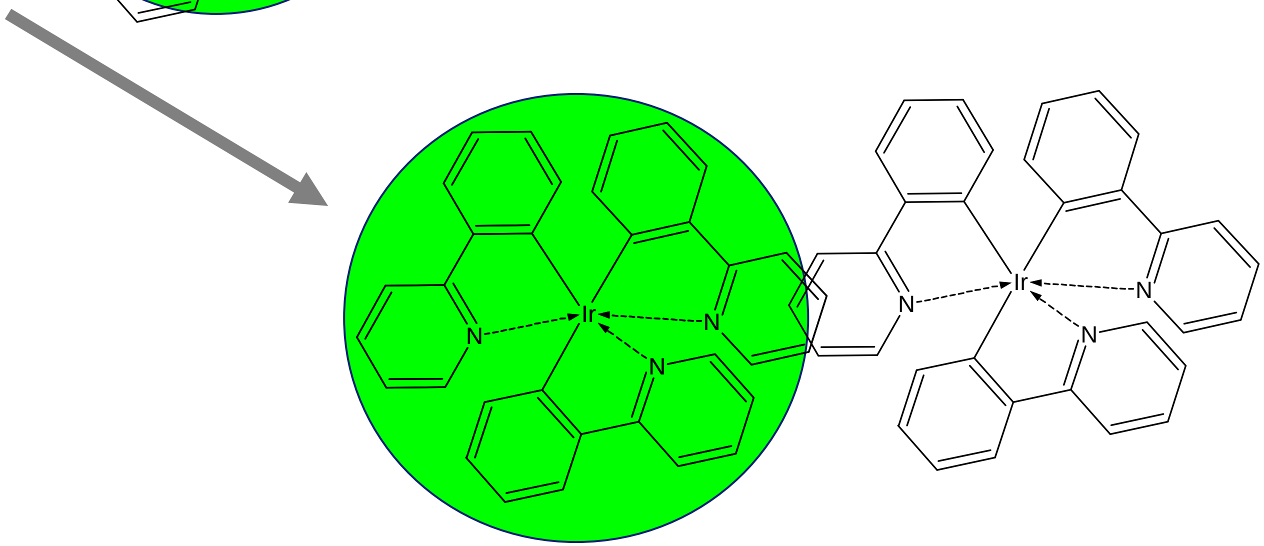


PHILIPS OLED structure optimisation : quenching II

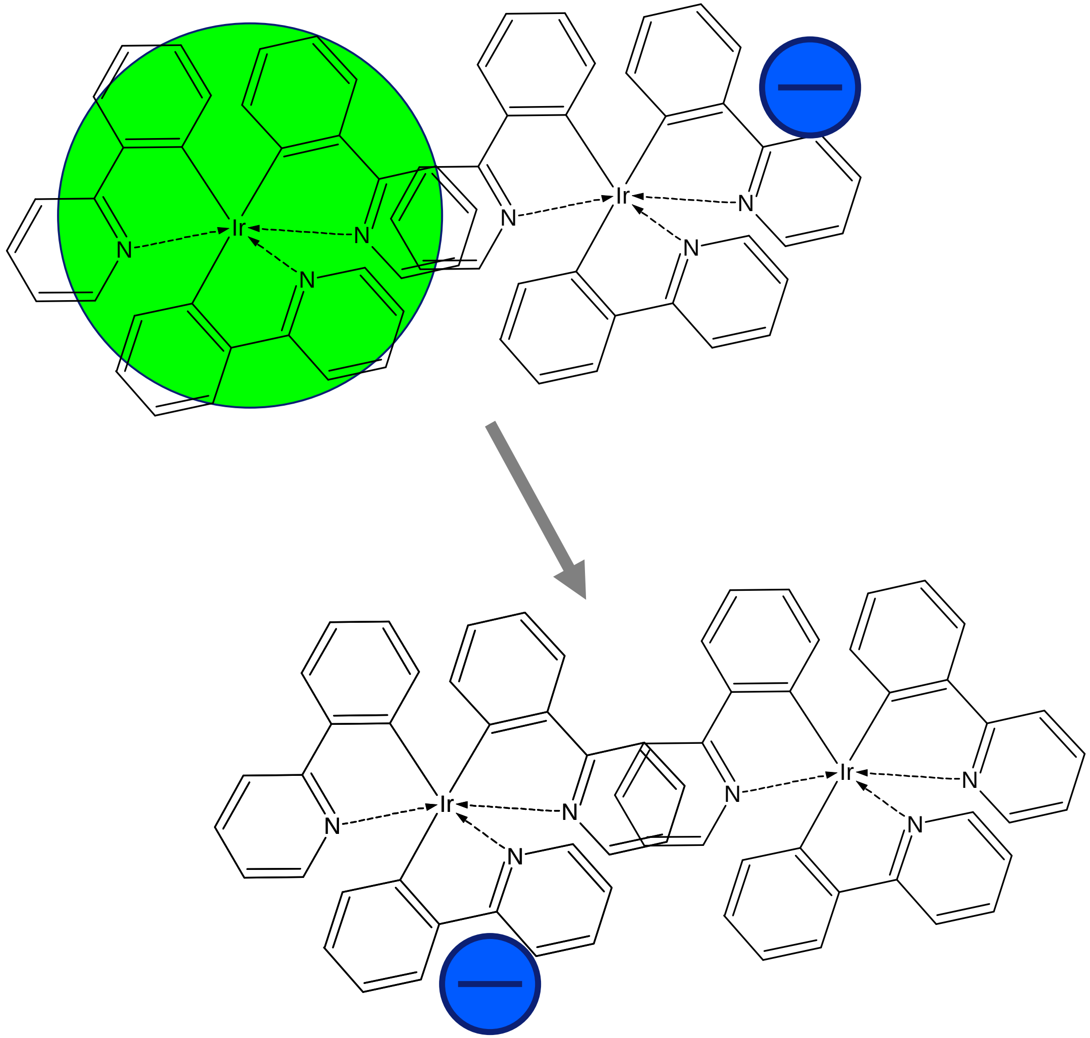


Triplet-triplet annilihation

$$^{3}M^{*} + {}^{3}M^{*} \text{ -> } {}^{3}M^{*} + M$$



PHILIPS OLED structure optimisation : quenching III

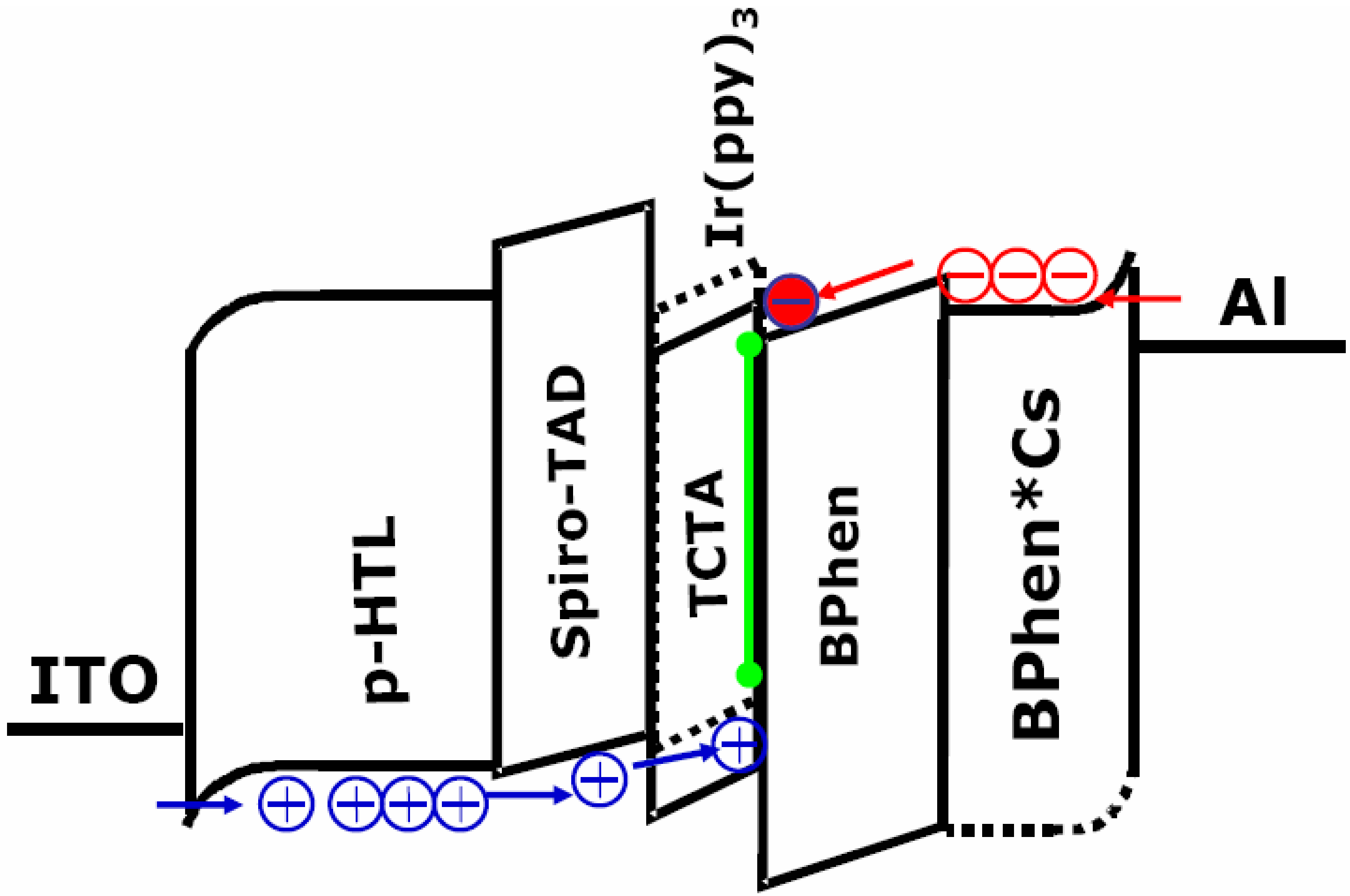


Quenching by charge carriers

$M^+ + {}^3M^* \text{->} M^+ + M$

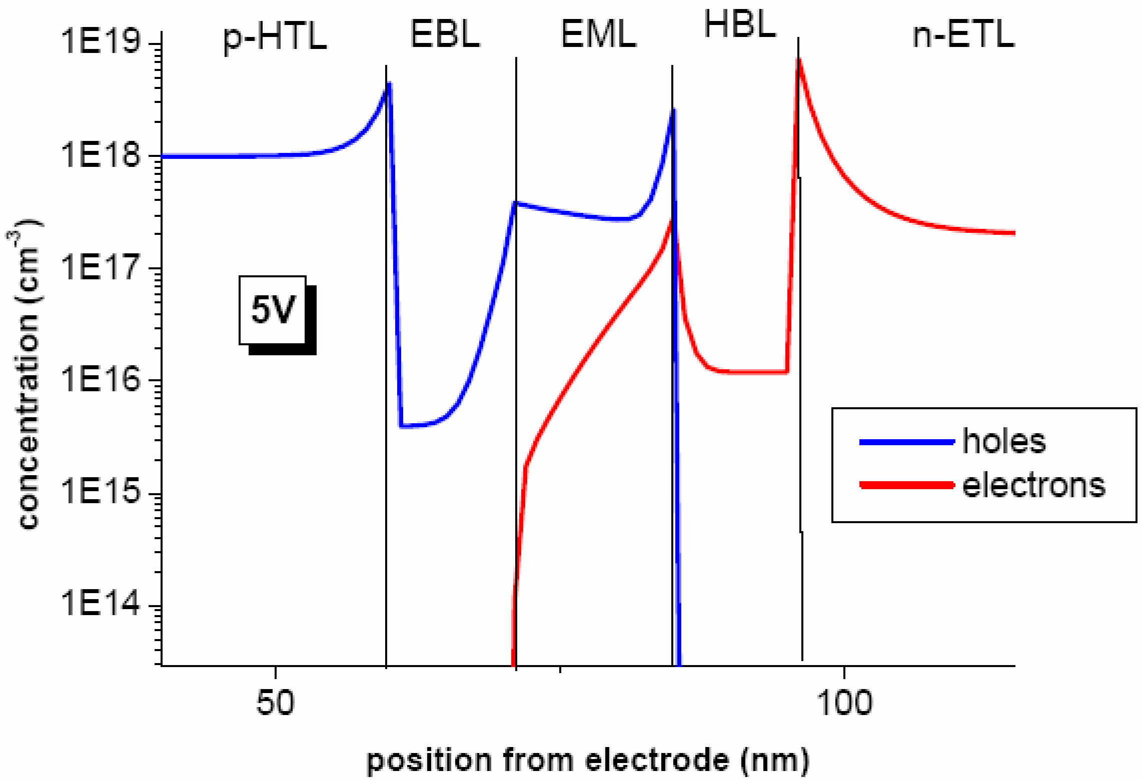
$M^- + {}^3M^* \text{->} M^- + M$

PHILIPS Simulation of charge densities



Martin Pfeiffer, IAPP Dresden, Feb. 2005

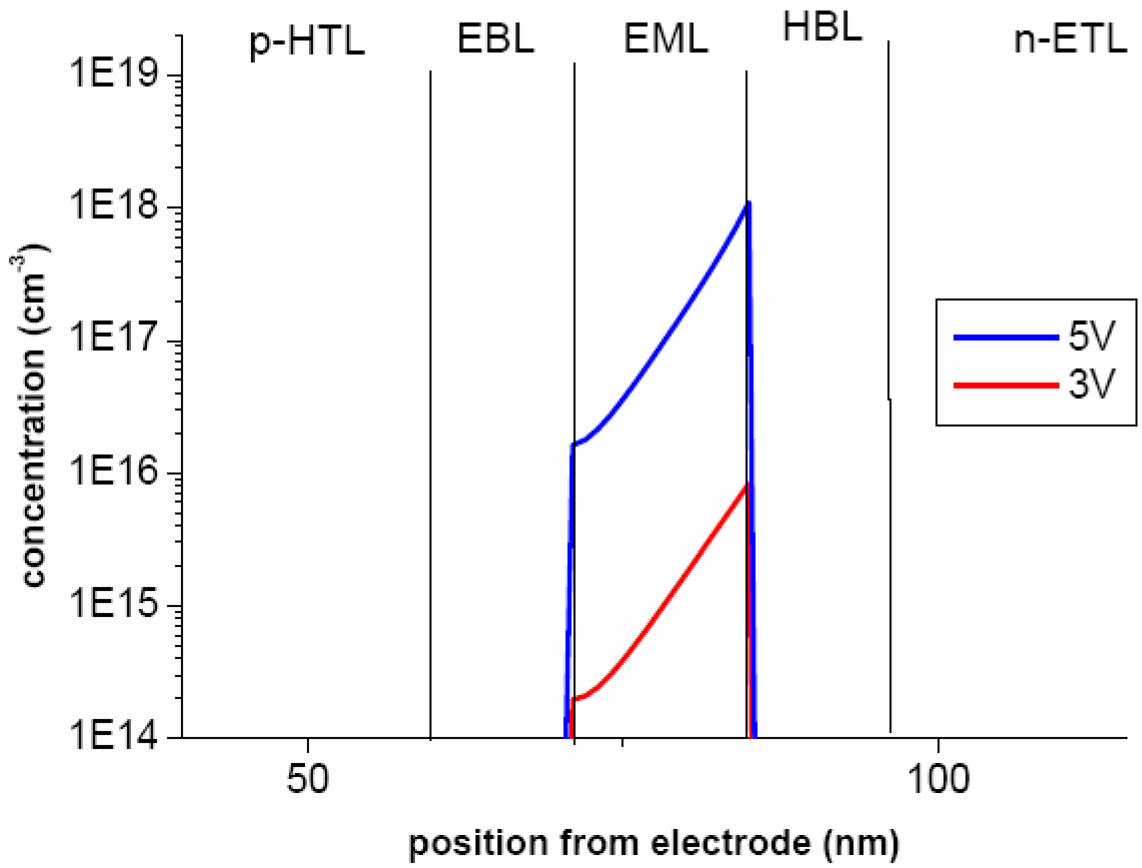
Simulation of charge densities



- surplus of holes in EML, especially at interface to HBL
- charge accumulation at interfaces of doped layers

Martin Pfeiffer, IAPP Dresden, Feb. 2005

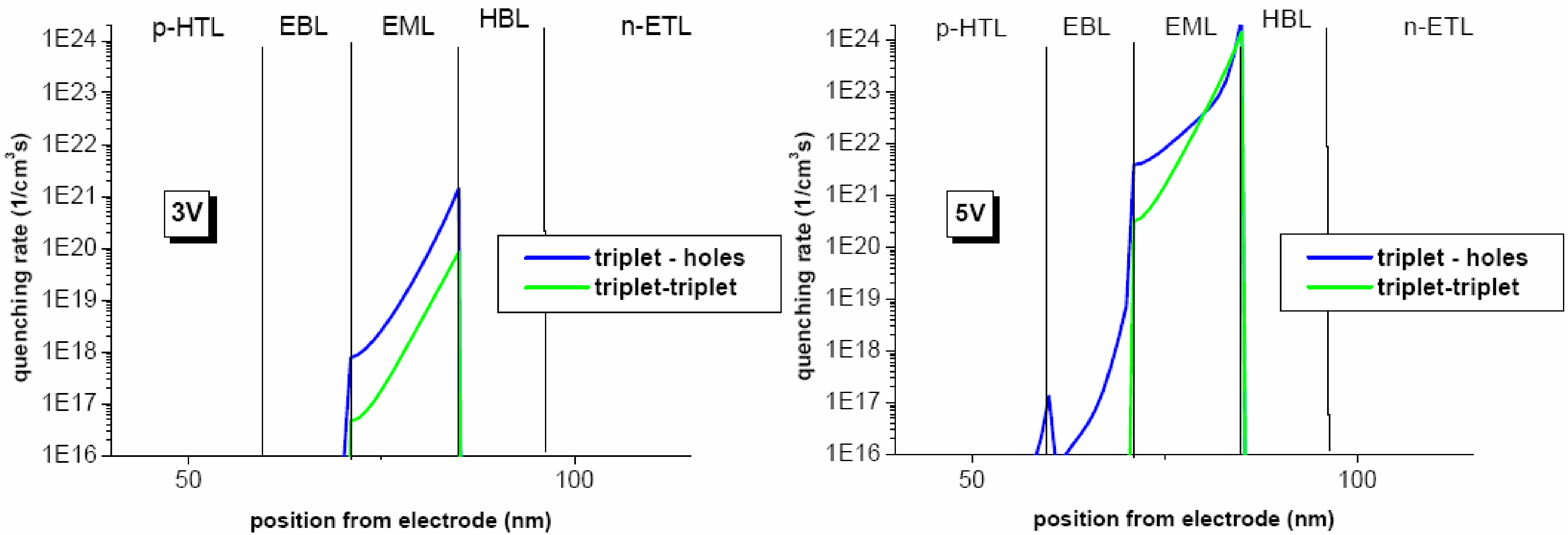
Simulation of triplet exciton distribution



- good confinement to EML
- main generation close to EML-HBL interface

Martin Pfeiffer, IAPP Dresden, Feb. 2005

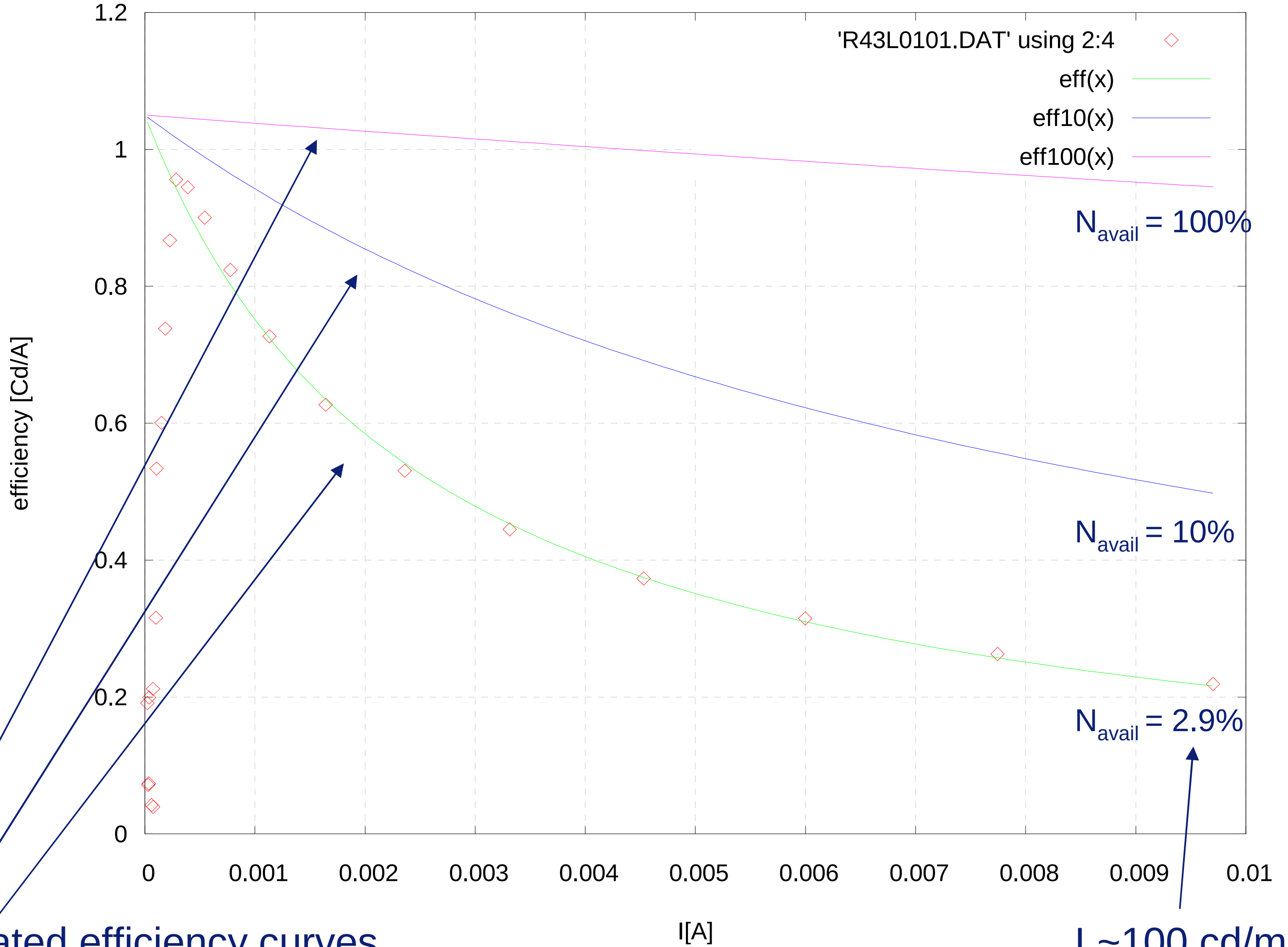
PHILIPS Simulation of bimolecular quenching processes



- some triplet-polaron quenching already at low brightness
- triplet-triplet-annihilation becomes more pronounced at high brightness

Martin Pfeiffer, IAPP Dresden, Feb. 2005

PHILIPS Saturation effects in a Eu^{3+} device



Simulated efficiency curves

L~100 cd/m2

Saturation effects in a Eu^{3+} device

- We are observing a quenching effect of the efficiency which is due to saturation of the excitation
- A simple model shows that only a fraction of the molecules in the emissive layer is excited
- most of the molecules do not participate in the excitation-emission process
- model:
    - already excited molecules cannot be excited again
    - The excitation rate is equal to the current density
- where are the excited molecules? At the interface of the emissive layer?
- why is there no excitation of the bulk emissive layer?

Saturation effects in a Eu^{3+} device

Device (I):

[+]

TPD (40 nm)

$Eu(DBM)_3BPhen$ (60 nm)

TAZ (10 nm)

[-].

Device (II):

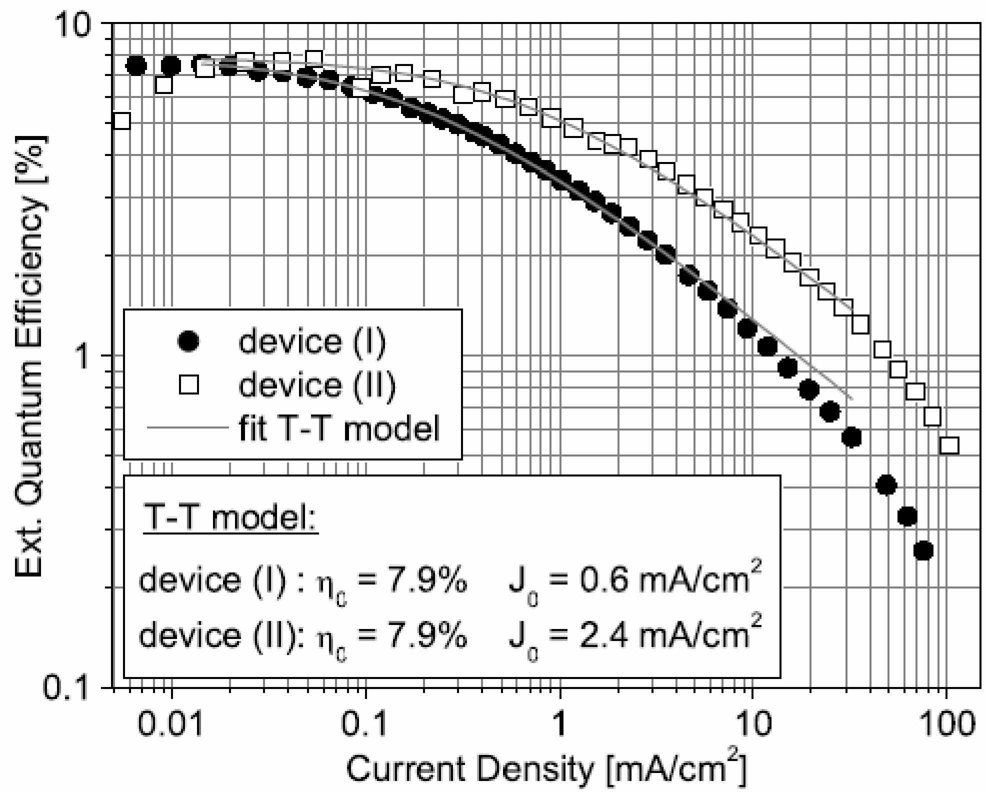
[+]

TPD (40 nm)

Eu(DBM)3BPhen:TPD(1:2, 20 nm) *E*u(DBM)3BPhen (40 nm)

TAZ (10 nm)

[-].



Exciton quenching in highly efficient europium-complex based OLEDs

T.W. Canzler and J. Kido, submitted for publication

Saturation effects in a Eu^{3+} device

Device structure:

[+]

TPD (40 nm)/ $Eu(DBM)_3BPhen$ (60 nm)/ TAZ (10 nm)

[-].

Possible improvements:

- TPD T_1: 19200 cm^{-1}
- DBM T_1 : 20300 cm^{-1}
- BPHEN T_1 : 21000 cm^{-1}
- TAZ T_1 : 22800 cm^{-1}

Use hole conductor with a T_1 > 21000 cm cm^{-1} to avoid loss of triplet excitons

Use appropriate matrix materials to improve charge transport in the emissive layer

Exciton quenching in highly efficient europium-complex based OLEDs

T.W. Canzler and J. Kido, submitted for publication

The roll-off of efficiency at high current densities

Dopant site saturation???

η_{ext} = c*1/J (J : current density)

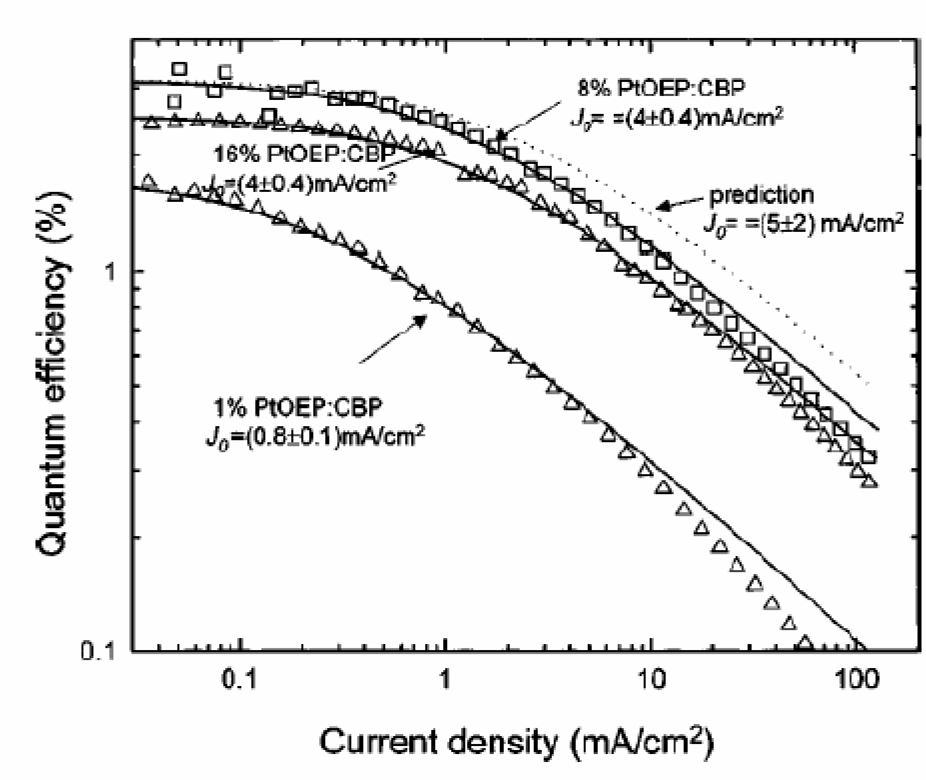
T-T annihilation : $\mathbf{T_1 + T_1 \rightarrow S_0 + S_1}$

$$\frac{\eta}{\eta_0} = \frac{J_0}{4J}\left(\sqrt{1+8\frac{J}{J_0}}-1\right)$$

η_0: quantum efficiency in the absence of TT annihilation

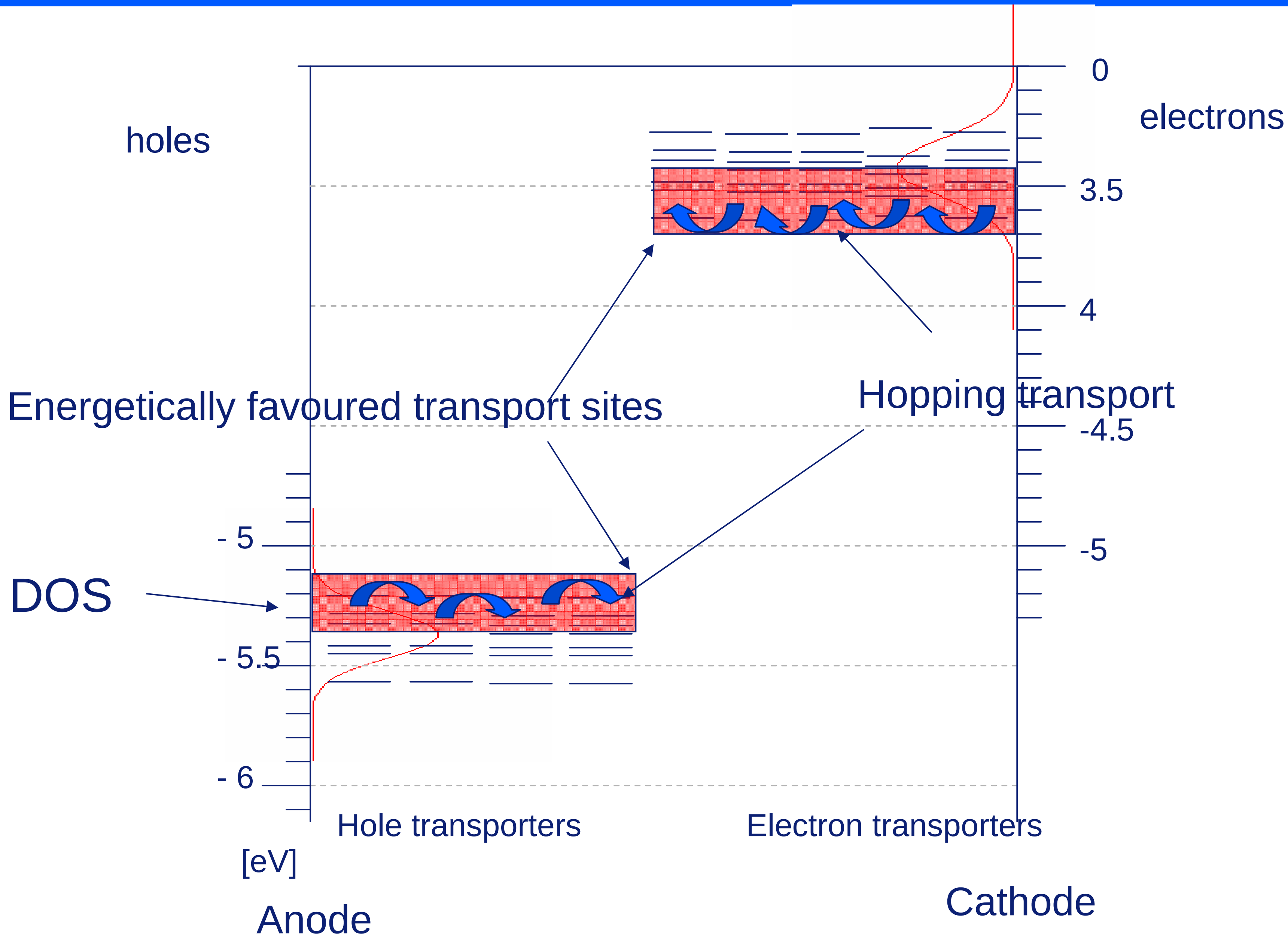
J_0: onset current density at $\eta = \eta_0/2$

$$J_0 = \frac{4qd}{k_{TT}\tau^2}$$



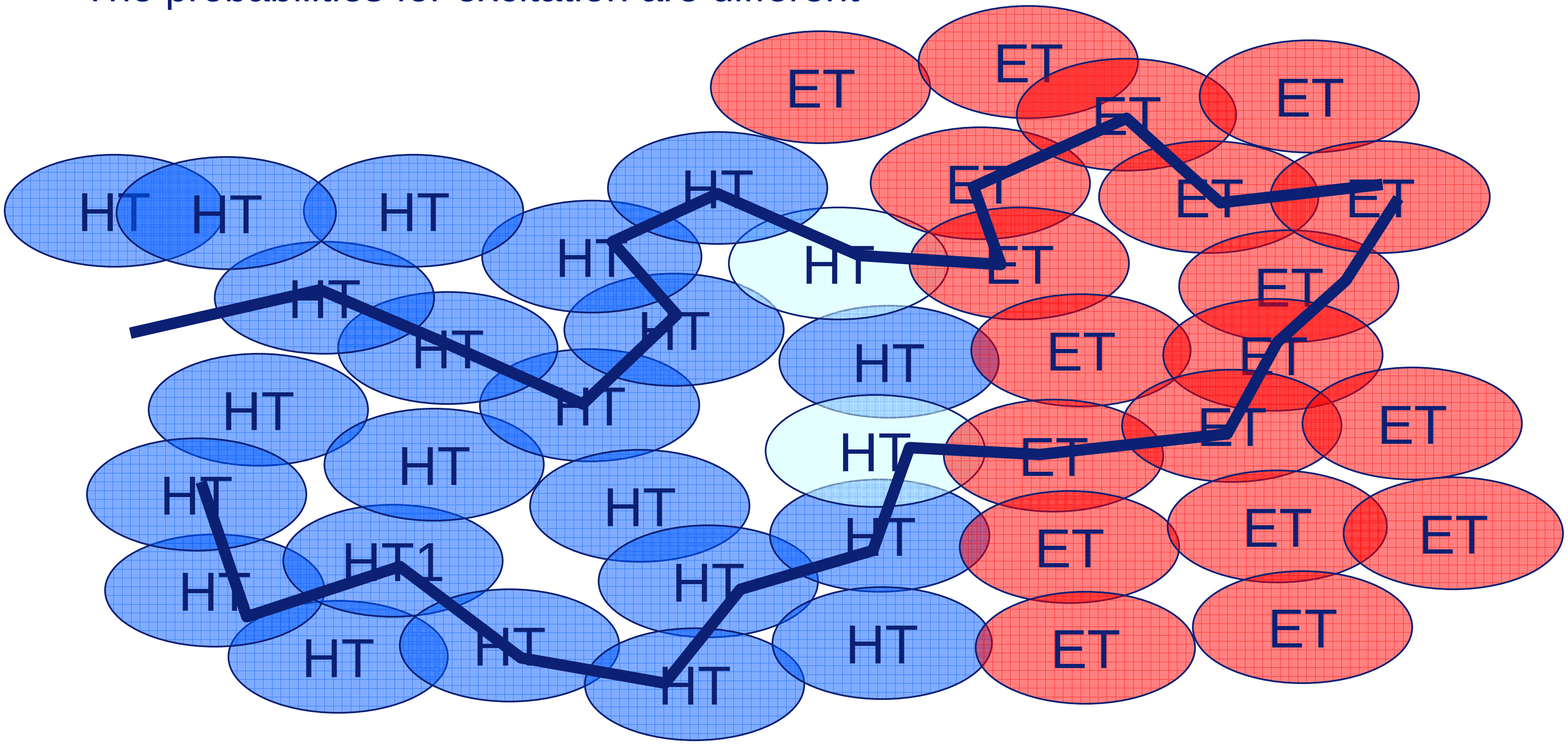
M. A. Baldo *et al*. Phys. Rev. B, 62, 10967 (2000)

Transport pathways in OLED I



Transport pathways in OLED II

- Due to disorder, charge transport along certain paths is more likely than for other paths
- The probability for molecules to receive charge is not equal
- The probabilities for excitation are different



Hopping transport along pathways

- Certain pathways favoured by energetics (disorder, DOS)
- Better recombination along these pathways, therefore higher probability to find a charge carrier on the molecules along this pathway
- Quenching due to charge-exciton interaction is stronger

- Prediction: matrix materials with high mobility are less affected because charge transport is better distributed (less disorder)

Lists of challenges

- New classes of efficient Eu^{3+} complexes wanted !
- High PL quantum efficiency
- All ligands should participate in the charge transport:
  - Appropriate HOMO and LUMO levels
  - Stable redox properties
  - Triplet level high enough

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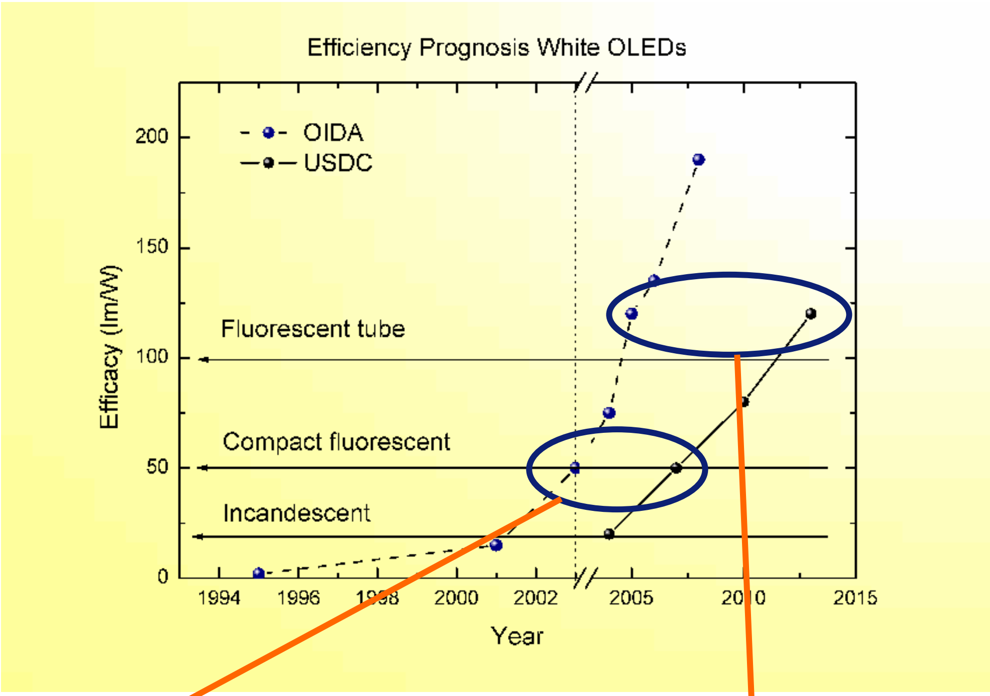
Conclusion

- Eu^{3+} are an interesting choice for highly efficient red emitters in OLEDS
- The long radiative lifetime enhances problems with T-T and charge-T annihilation considerably
- Not so many ligands have been tried yet
- No concentrated effort for better complexes so far
- Many opportunities if knowledge from OLED theory is incorporated into design
- Quenching problems have to be solved for other triplet emitters as well (but on a lower level)
- Good test environment for well-distributed excitation

Prime importance of efficiency

- Efficiency of prime importance, especially for general lighting applications
- Saves electrical power for lighting
- Improves COO balance for OLEDs (lm/€)
- Minimizes secondary problems (e.g. lifetime problems through self-heating)



Energy saving bulb efficiency in 2-4 years

New efficiency record in ca. 3-8 years

The lighting challenge

Already achieved

>100 lm/W
(green)

>50000h

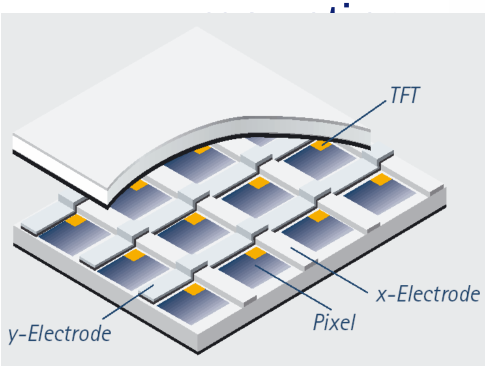
>$1*10^6$ cd/m²

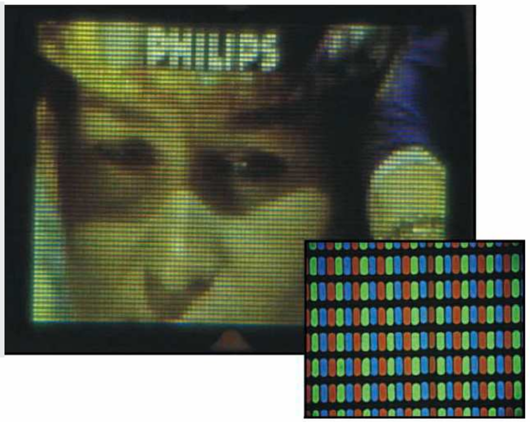
Lighting requirements

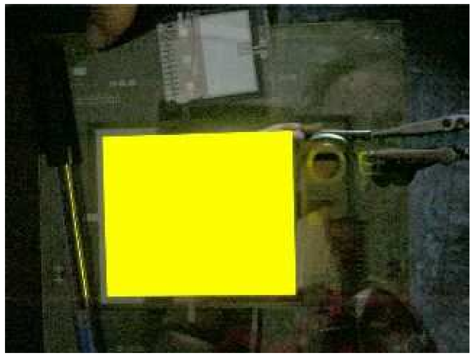
1000cd/m²
CRI >80
>10000h
> 35lm/W

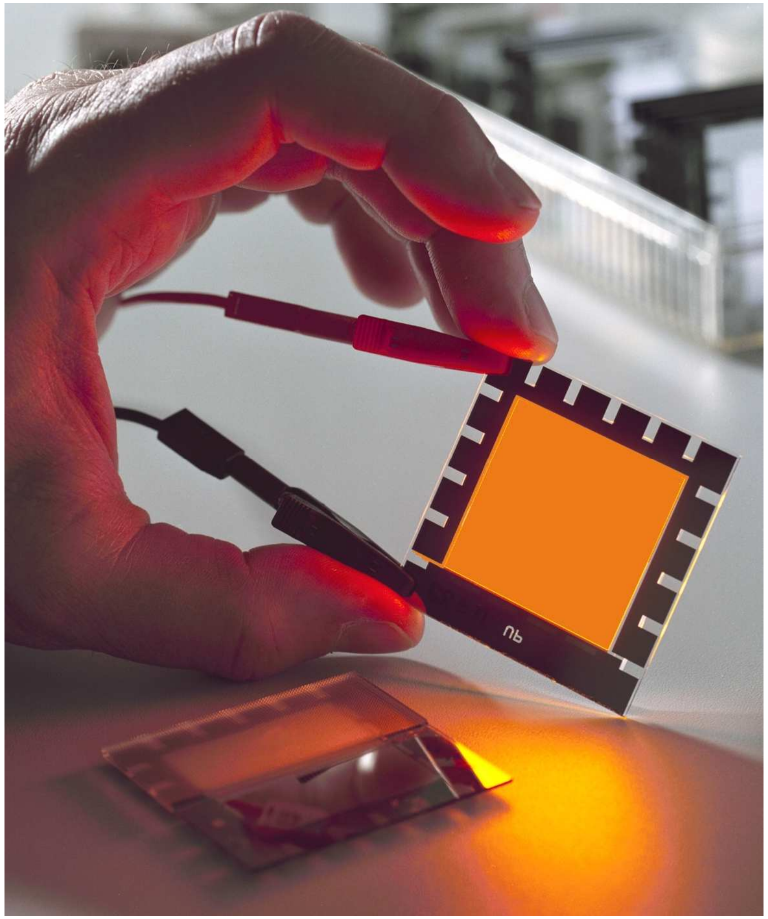
Differences Displays-Lighting

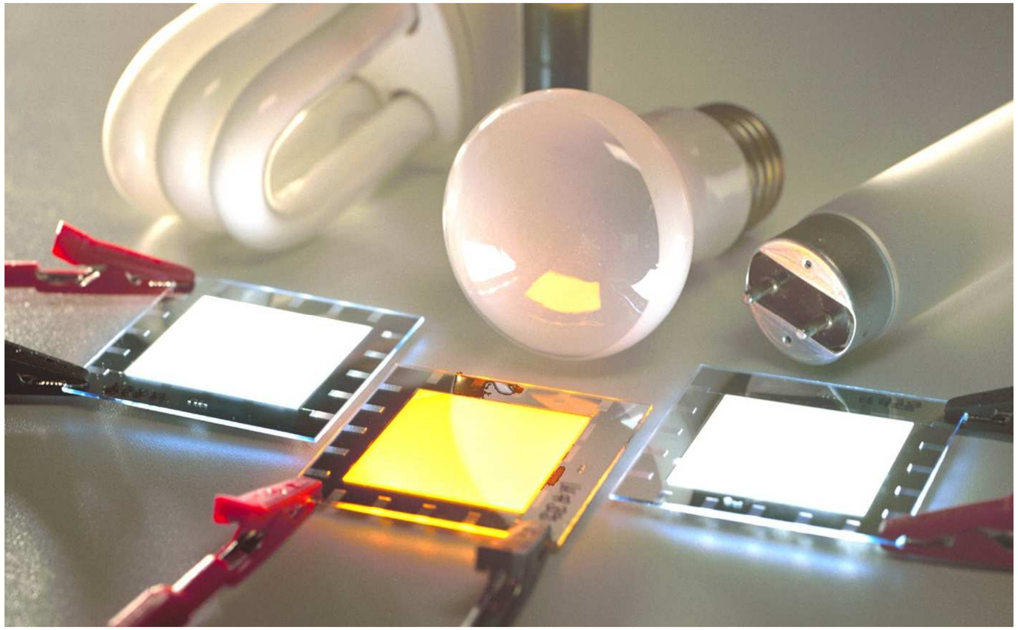
- Displays
  - Pure colors (RGB)
  - Pixelated (<200µm)
  - typical 100cd/m²
  - Lifetime 5000h
  - High importance of peripheral components (driver IC, connections.
- Lighting applications
  - 1000cd/m²
  - Lifetime >10000h
  - White light (high CRI)
  - “Large” area homogeneous
  - High efficiency











High efficiency blue-green

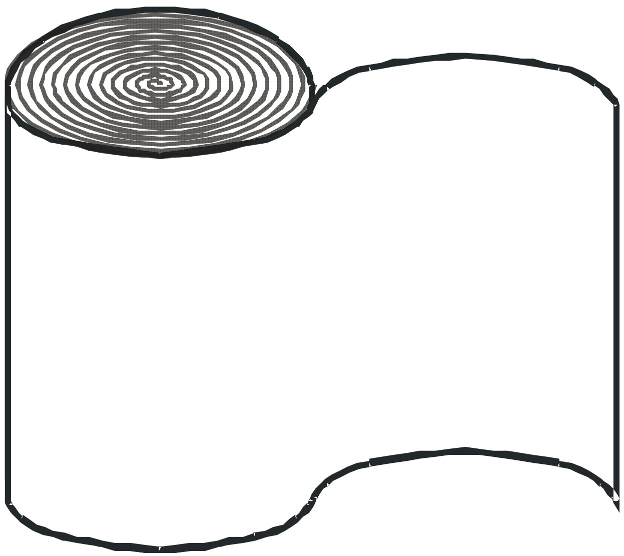
High efficiency white

High efficiency orange

Potential starting markets

- Automotive
  - decoration
  - interior
- Signaling
  - Advertising
  - Emergency exits
- Luminance applications
  - Decoration
  - Accent lighting

The ultimate lightfoil



- bright
- flexible
- efficient
- tunable
- long lived

... for any lighting application

OLED Application advantages for Lighting

- Transparent, mirror-like or white appearance
- Thin, flat, lightweight
- “Green” product (energy efficient, recylable)
- Low voltage technology
- Potentially cheap fabrication
- (Potentially) High efficiency
- Large area diffuse light source
- Fast switch-on
- Fully dimmable
- Many colors, incl. different white’s
- Form freedom in design

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Energy efficiency will matter a lot in the future…