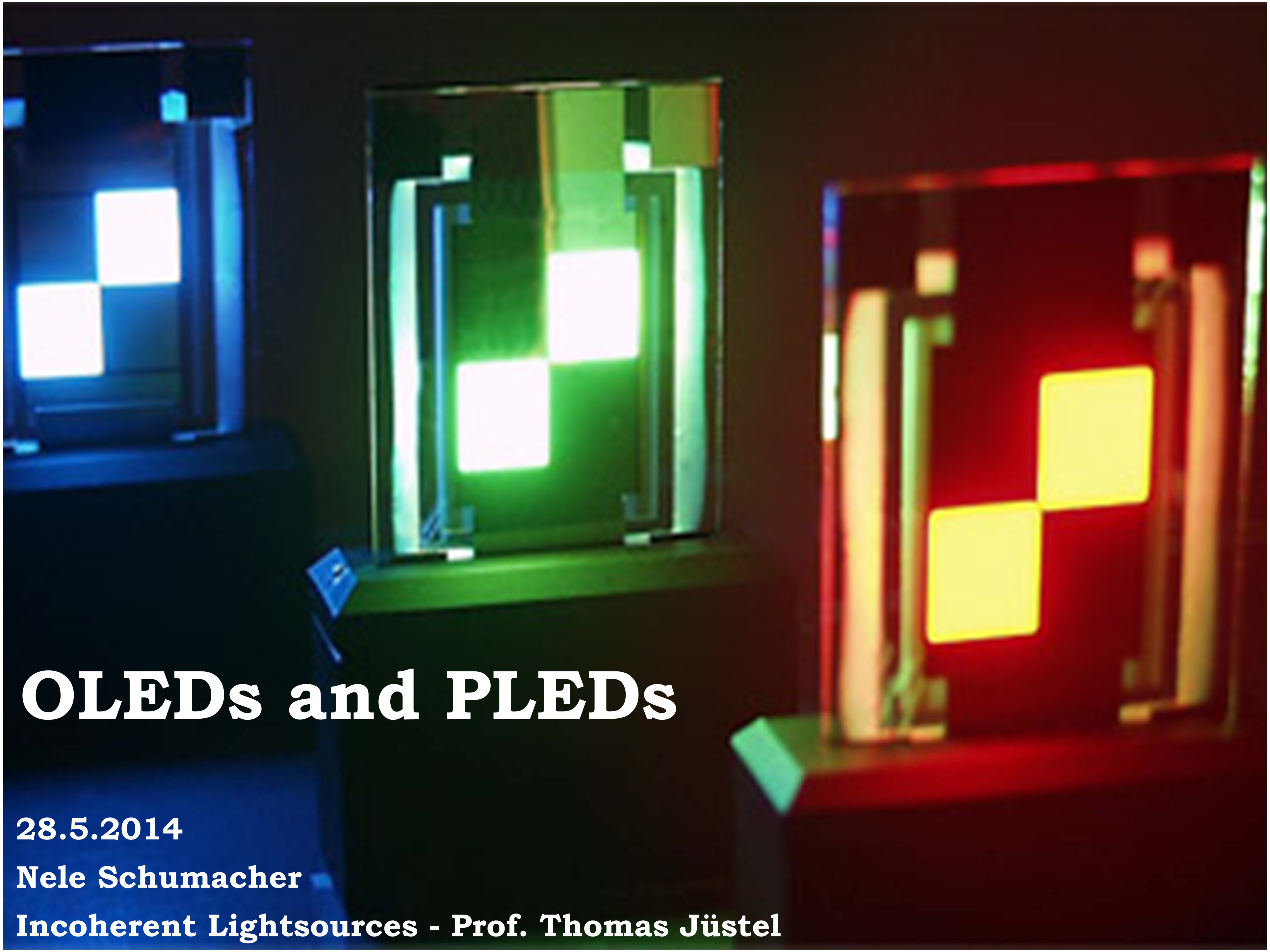


OLEDs and PLEDs

28.5.2014

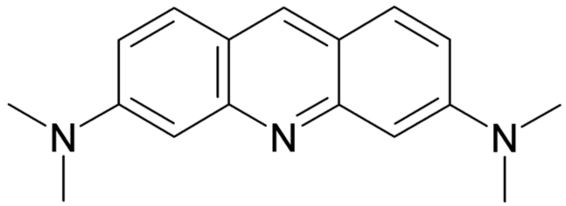
Nele Schumacher

Incoherent Lightsources - Prof. Thomas Jüstel

Contents

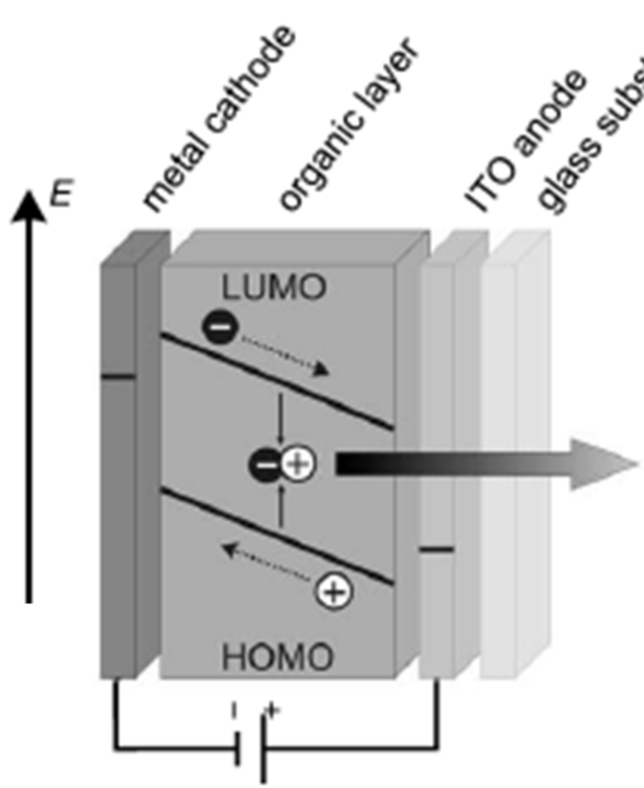
1. History

- 1953: AC electroluminescence of acridine orange was observed

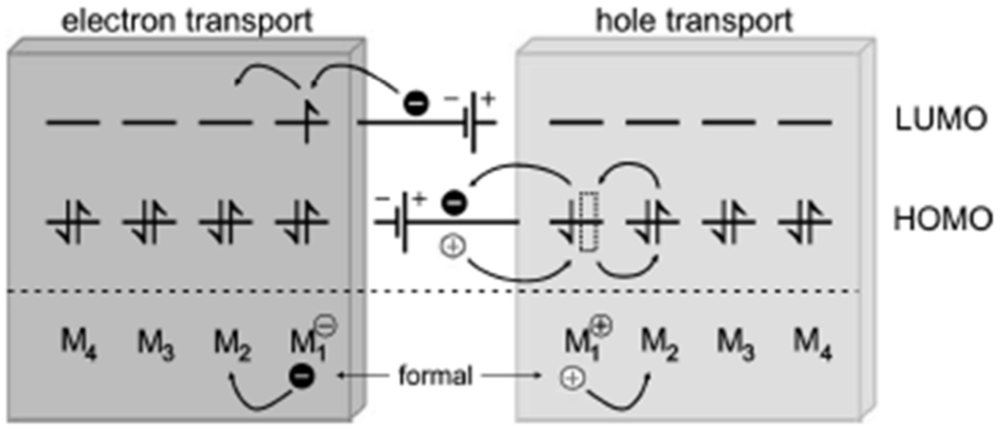


- 1960's: DC electroluminescence of anthracene (400 V)
- 1975: Electroluminescence from polymers was observed
- 1987 - Breakthrough: multilayered structure of an emissive layer between hole transporting and electron transporting layer (10 V)

2. Working principle
2.1. Single layer OLEDs



Hopping process:



Monatshefte für Chemie **137** (2006) 811-824.

2.1. Single layer OLEDs

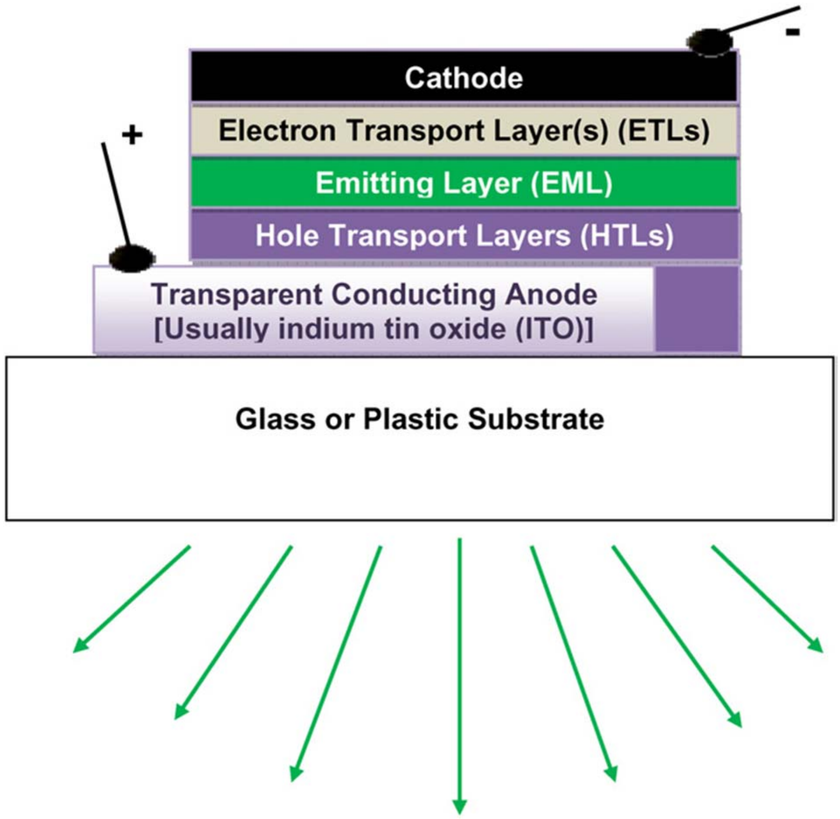
- Problems:
  - No balanced charge injection into organic layer
  - Different carrier mobilities of electrons and holes through the organic layer
  - Quenching processes
    - Exciton quenching close to electrodes
    - Passing of charges through layer from electrode to electrode without recombination (dark current)

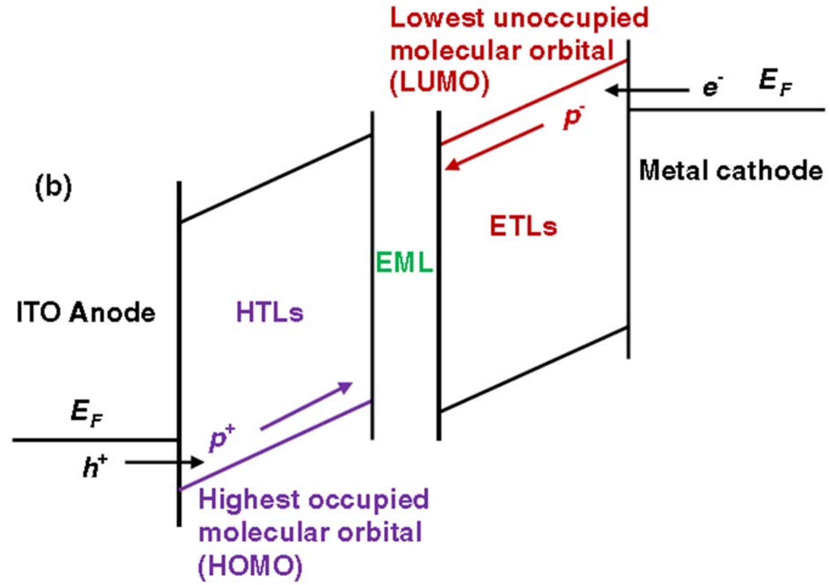
→ **Problems can be overcome by multilayer OLEDs**:

Recombination zone in the middle of the emissive layer

2. Working principle

2.2. Multilayer OLEDs





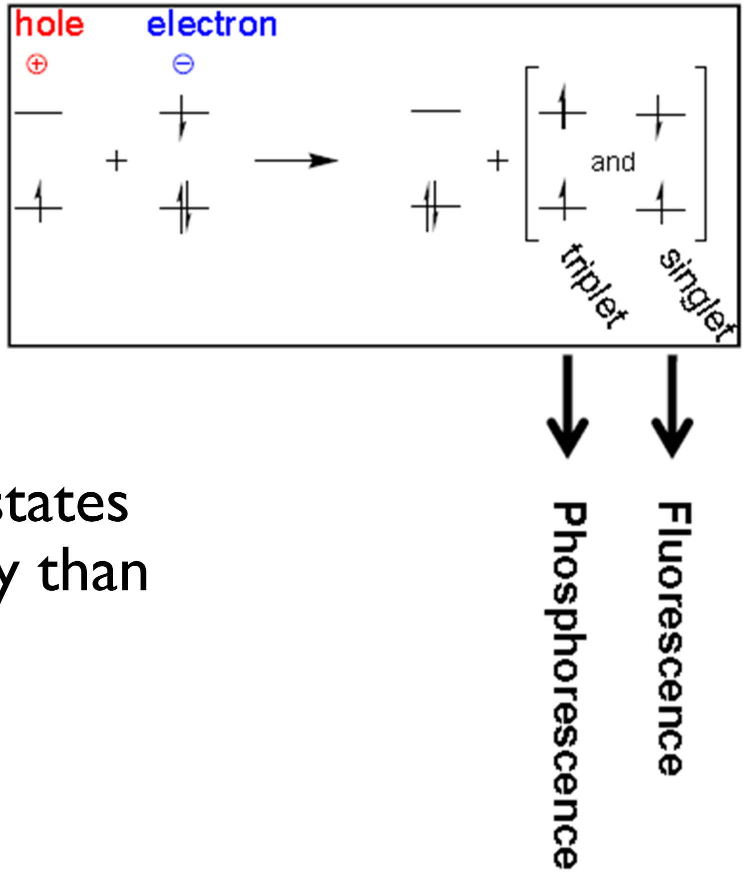
Journal of Physics D: Applieds Physics **41** (2008) 133001.

3. Materials
3.1. Fluorescent and phosphorescent materials

Fluorescence or phosphorescence materials?

- Energy level of ground state: singlet state
- 2 different energy levels of excited states:
  - Singlet excitons: antisymmetric spin, total spin S = 0
    - Transition to singlet ground state: allowed
    - **Fluorescence** within nanoseconds
  - Triplet excitons: symmetric spin, S = 1
    - Transition to singlet ground state: forbidden
    - **Phosphorescence** within microseconds to seconds

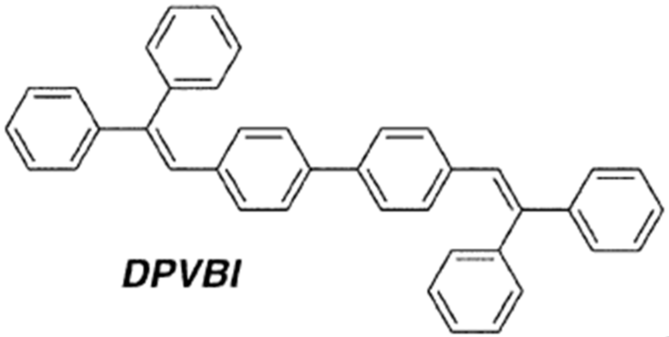
3.1. Fluorescent and phosphorescent materials



- Electrons and holes form triplet states with a threefold higher probability than singlet states
  - 75 % results in phosphorescence
  - 25 % of injected charges results in luminescence

Lecture script „*incoherent light sources*“, Prof. Jüstel

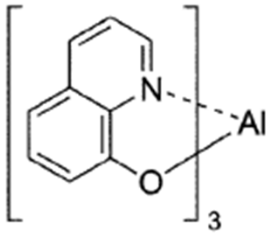
3.1.1. Fluorescent materials



DPVBI

4,4′-Bis(2,2-diphenylethene-1-yl)diphenyl

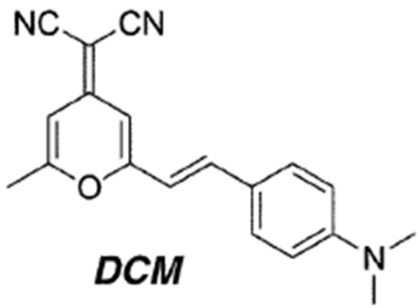
blue



Alq3

Tris(8-oxychinolato)aluminum

green

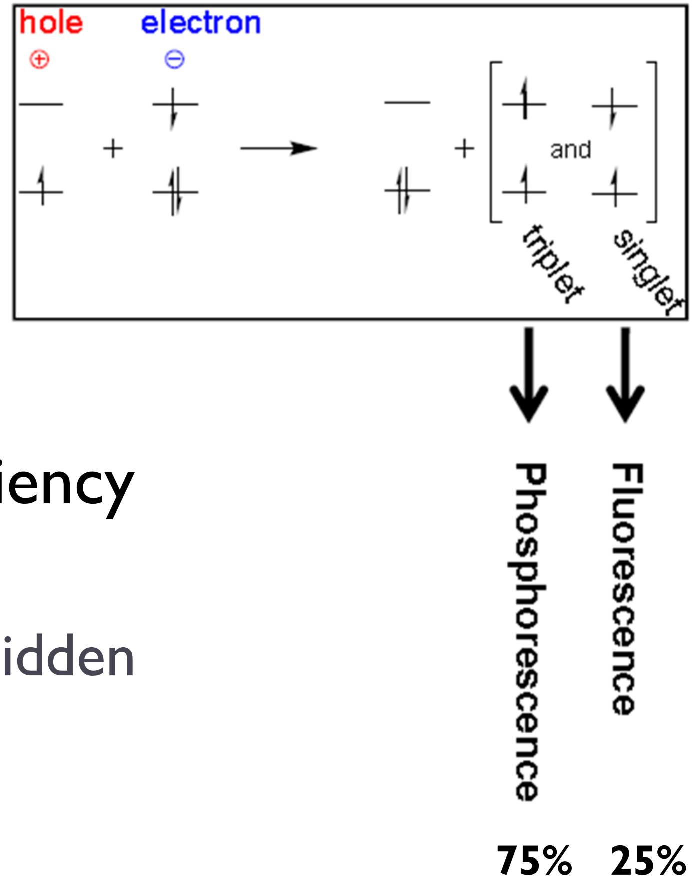


DCM

4-(Dicyanomethylene)-2-methyl-6
(*p*-dimethylaminostyryl)-4*H*-pyrane

red

3.1.1. Fluorescent materials



- Limited internal quantum efficiency (25 %)
  - decay of triplet excitons is forbidden
    - Long lifetime of excitons
    - Nearly no phosphorescence
  - Only formation of singlet excitons results in radiative emission

3.1.2. Phosphorescent materials

- Improved materials: Transition metal compounds with organic ligands (guests) into host materials (organic molecules or polymers)
- Strong spin-orbit coupling: Fast intersystem crossing (ISC)
  - Mixing the singlet and triplet character of excited states
  - Reduced lifetime of triplet state excitons
  - Enhanced phosphorescence, higher external quantum efficiencies
- Used transition metals: **Iridium**, platinum, osmium, ruthenium

3.1.2. Phosphorescent materials

Observed transitions:

- d-d – transitions (forbidden, weak)
- Intra-ligand π-π* transitions
- MLCT transition from d-orbitals to π*
  - Emissive transition observed in d^6 and d^8 systems (→ Ir^{3+})
- LMCT in complexes with metal atoms in high oxidation states or in d^{10} complexes

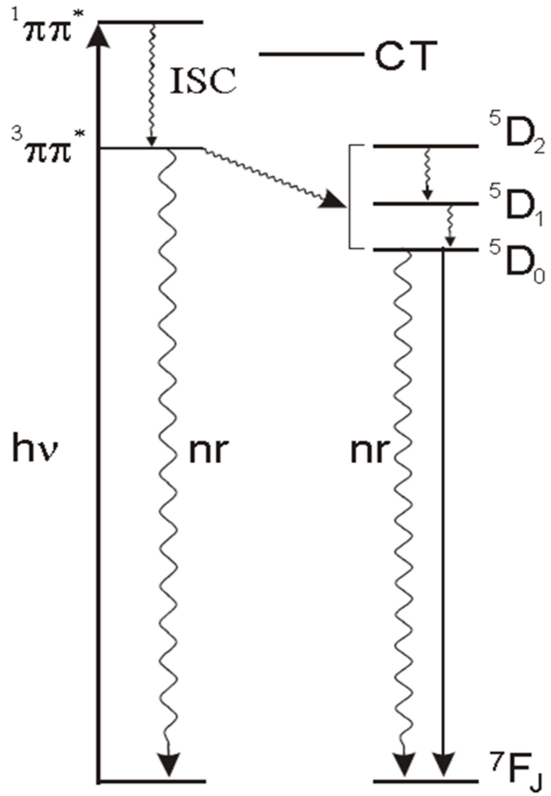
3.1.2. Phosphorescent materials

Transfer processes in host materials doped with phosphorescent materials:

- LMCT from host to guest
- Triplet level of host must be larger than triplet level of the guest

→ Limited number of host materials

Energy level diagramm of Eu^{3+} complexes:



Lecture script „*incoherent light sources*“, Prof. Jüstel

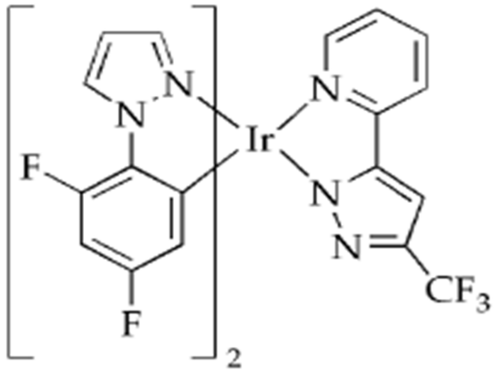
3.1.2. Phosphorescent materials

Material selection:

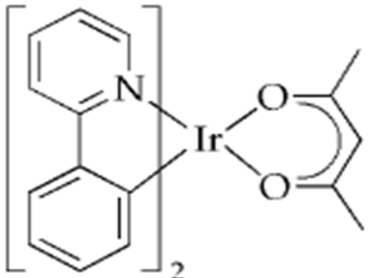
- Energies of the HOMO play major role
- Colour tuning by:
  - Adjusting the metal and ligand orbitals by changing the substituents
  - Changing ligand structures
- Most promising class: Iridium complexes

3.1.2. Phosphorescent materials

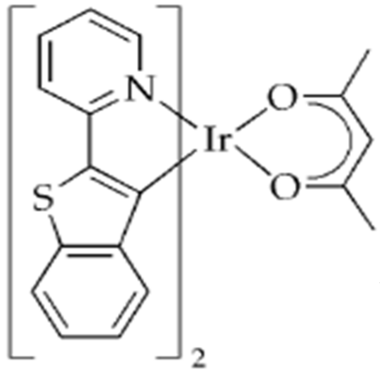
Examples of phosphorescent iridium complexes:



emitting at 455 nm



emitting at 515 nm



emitting at 612 nm

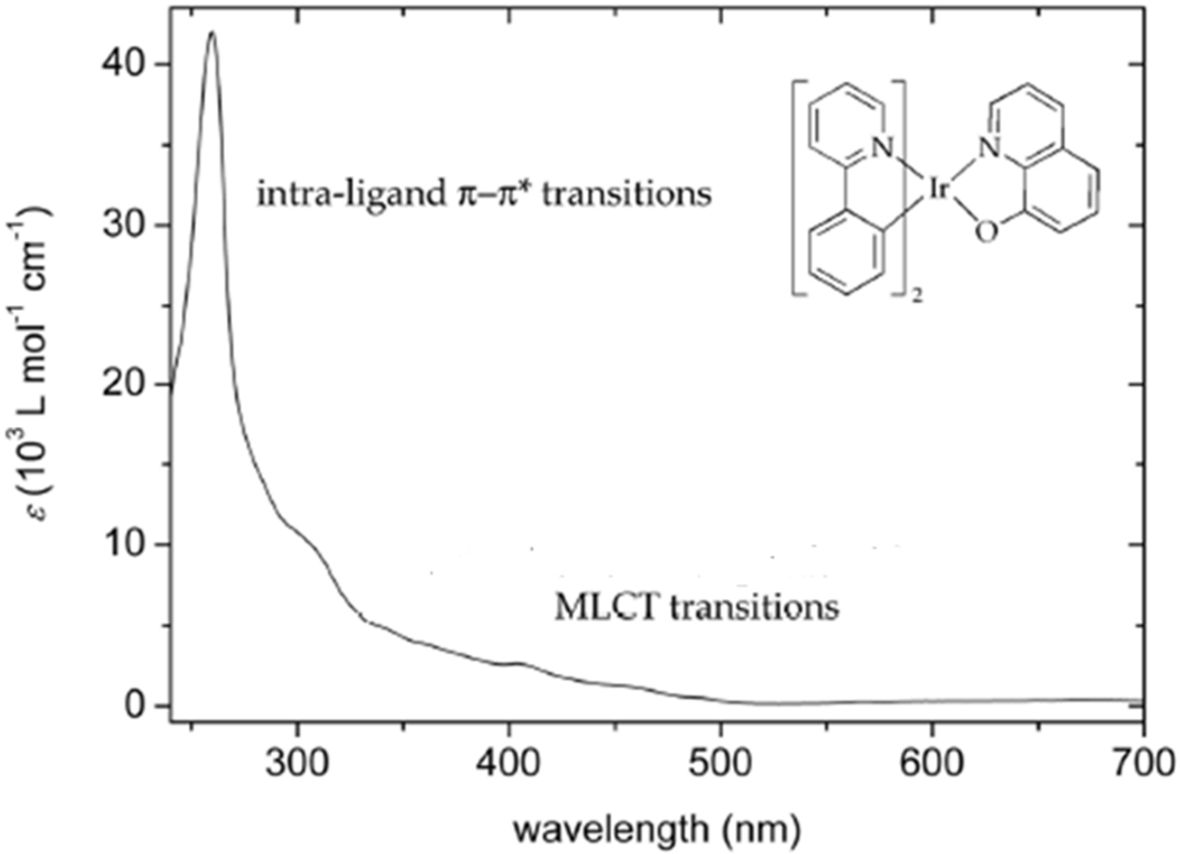
International Journal of Molecular Sciences **9** (2008) 1527-1547.

Ir^{3+}: [Xe]$4d^{14}5d^{6}$

- strong spin-orbit coupling, high crystal field splitting
- only low spin complexes
  - Very high crystal field splitting energy → very stable complexes!

3.1.2. Phosphorescent materials

Absorption spectra of Ir(III) compounds

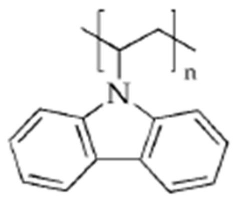


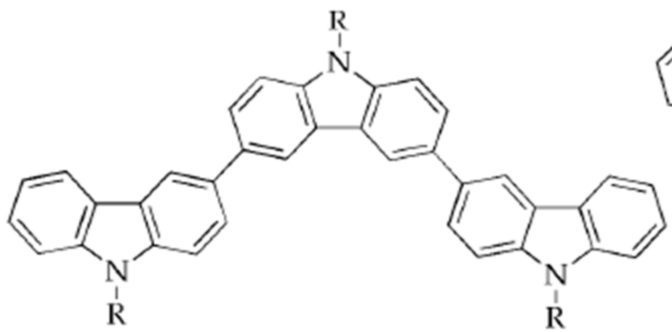
International Journal of Molecular Sciences **9** (2008) 1527-1547.

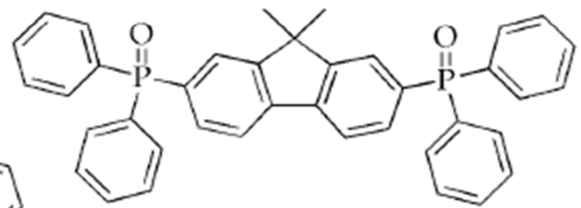
3. Materials

3.2. Host materials

- Requirements:
  - HOMO/LUMO levels need to be good charge injectors
  - Chemical and morphological stable
  - Triplet level of host material must be larger than triplet level of the guest

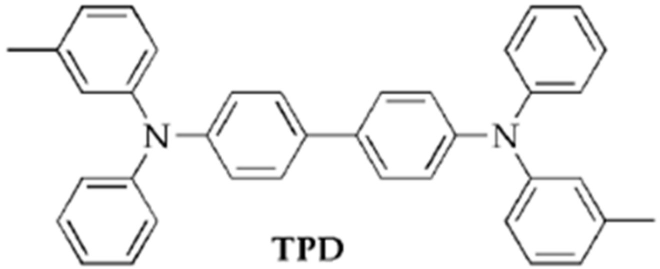






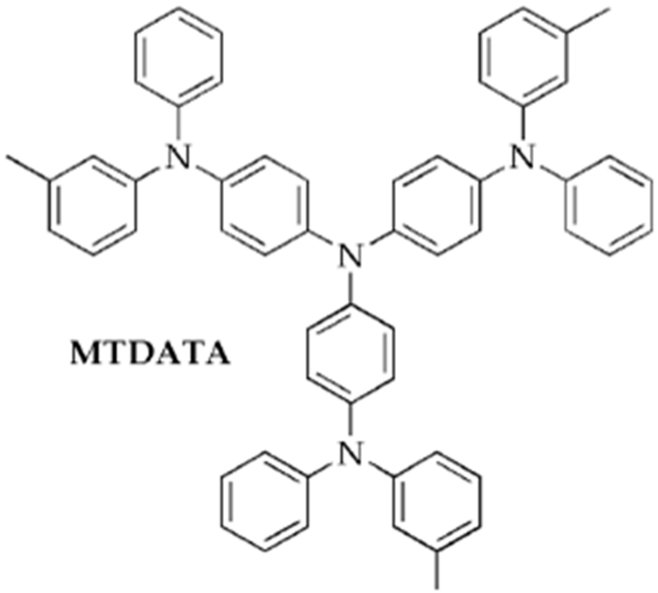
3. Materials

3.3. Hole transport materials



TPD

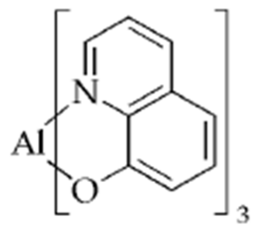
TPD = *N,N'*-diphenyl-*N,N'*-*bis*(*m*-tolyl)-1,1'-
biphenyl-4,4'-diamine



MTDATA

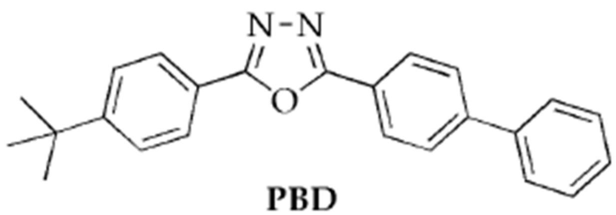
MTDATA = *m*-methyl-*tris*(diphenylamine)triphenylamin

3.4. Electron transport materials



Alq$_3$

Alq3 = aluminum quinolinolate



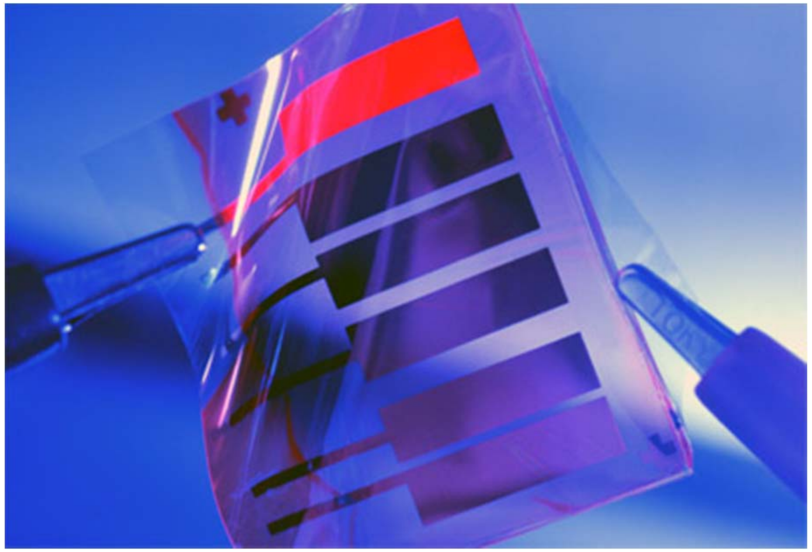
PBD = (2-(4-biphenyl)-5-(4-
tert-butylphenyl)-1,3,4-oxadiazol)

3.5. Polymer LEDs (PLEDs)

- Several problems for OLEDs are present
  - Complexity of device fabrication
  - Expensive fabrication
  - Insufficient fine-dispersion of dopant in the host material
  - Phase separation

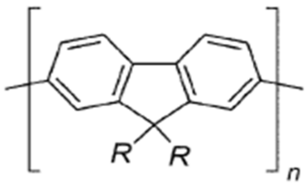
→ **Solution: Incorporation of phosphorescent guest into polymers!**

3.5. Polymer LEDs (PLEDs)



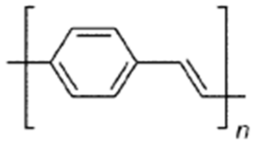
- Advantages of PLEDs:
  - Good processability
  - Good film forming properties
  - Low cost manufacturing processes from solution (spin coating)

3.5. Polymer LEDs (PLEDs)



Poly(fluorene)

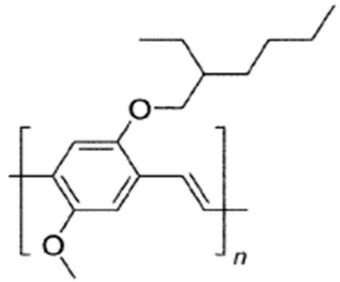
blue



PPV

Poly(*p*-phenylenvinylene)

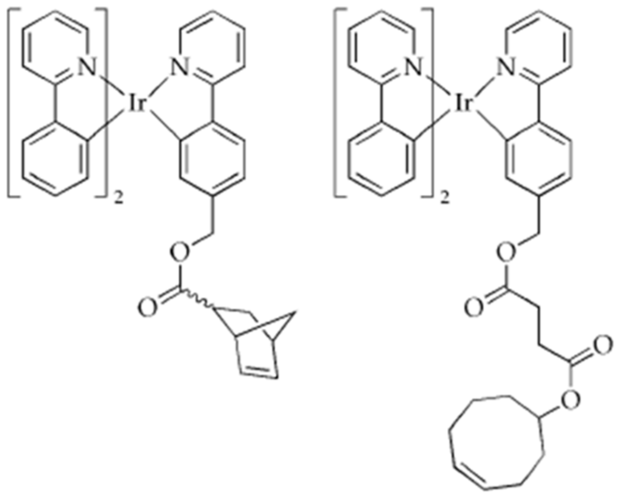
green



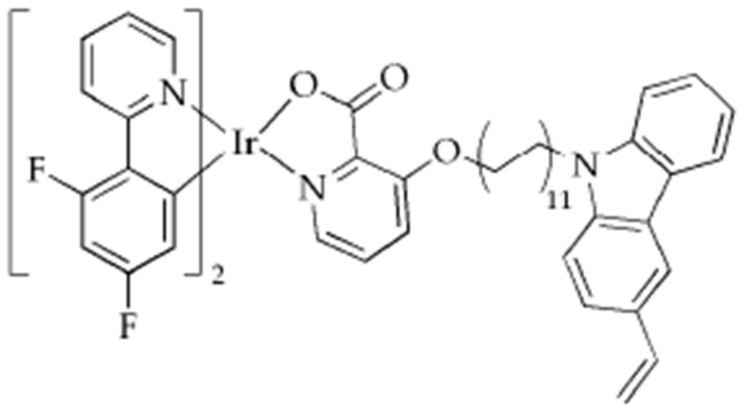
DPVBI

Poly[(2-(2-ethylhexyloxy)-5-methoxy-*p*-phenylen)vinylene]

red



for ROMP polymerization



for radical polymerization techniques

4. Preparation of multilayer devices

- Vacuum sublimation
  - Multilayer structures can be easily built up
  - Additional final purification step
  - Limited to vaporisable low molecular weight materials
  - Expensive technology

- Solution processing techniques (e. g. spincoating)
  - For polymeric materials: less expensive
  - Multilayer production quite difficult: previously deposited layers needs to be resistant against the solvent used to deposit the next layers
  - Best strategy: Additional photocrosslinking step resulting in a insoluble network

5. Advantages and disadvantages
5.1. Advantages

- Show self-emission (LCDs filter backlight)
- Broad colour ranges and better colour reproduction
- High resolution and dark contrasts (LCD cannot show true black)
- Need less space, thin display molecules
- Lightweight and flexible plastic substrates (roll-up displays)
- Faster display response times

5. Advantages and disadvantages
5.2. Disadvantages

- Colour balance: blue OLED degrades more rapidly than the other colours
- Limited lifetime of organic materials (blue OLED, 5 years, 8h a day: half of original brightness)
- LCDs have similar properties, additionally higher stability and longevity
- No mass production yet, LCD cheaper in production
- Water damages the organic materials → good sealing is very important
- Power consumption:
  - If image is primarily black: less power is needed than in a LCD
  - If image is primarily white: more power is needed than in a LCD

6. Future aspects

- OLEDs might become printable on a substrate → cheaper
- Flexible mobile phones „Philips Fluid“
- Transparent OLEDs

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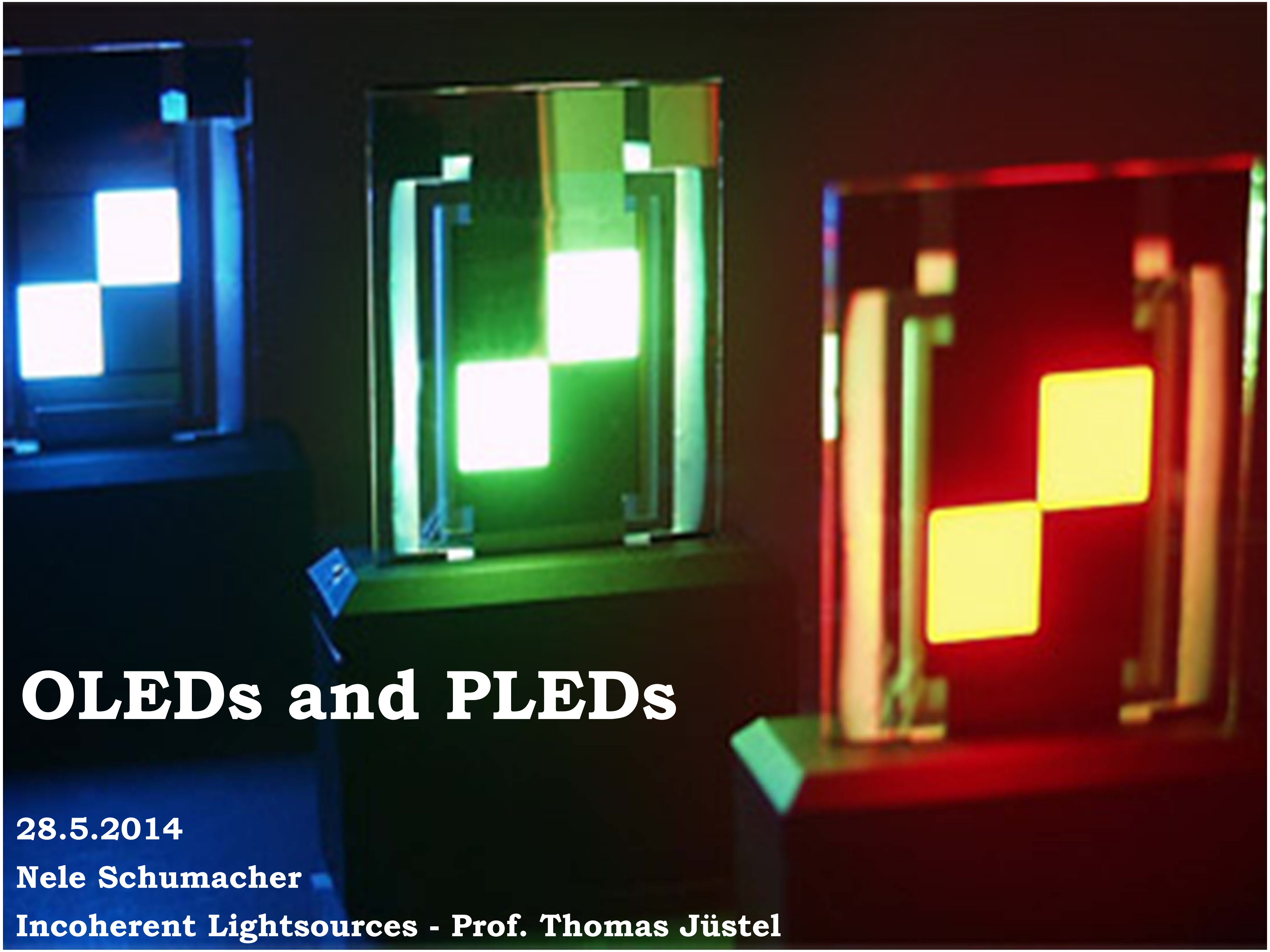
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