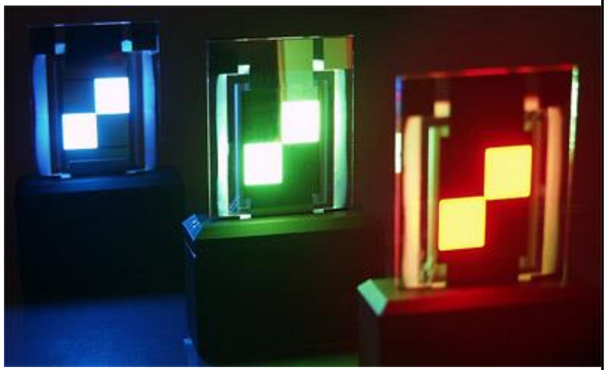
10. OLEDs and PLEDs

Content

10.1 Historical Development

Some milestones

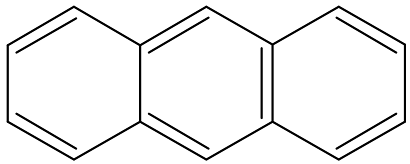
- 1953 Observation of the electroluminescence of acridine orange
- 1961 Thermally activated delayed fluorescence (TADF) from Eosin
- 1963 Report of EL in anthracene single crystals
- 1987 Eastman Kodak: OLED with [Al(8-hydroxychinolinate)$_3$]
- 1990 Cambridge Univ.: Polymer based OLED with poly(p-phenylene vinylene)
- 1999 First report on Ir^{3+} complexes: fac-[Ir(ppy)$_3$)]^0
- 2009 Universal Display Corp. 102 lm/W
  Novaled/TU Dresden 90 lm/W
  Konica 64 lm/W
  Kodak 56 lm/W
- 2012 Samsung: 55 inch OLED TV
- 2019 LG: 88 inch OLED TV with 8K
- 2020 Cynora: Efficient & stable blue OLED emitter



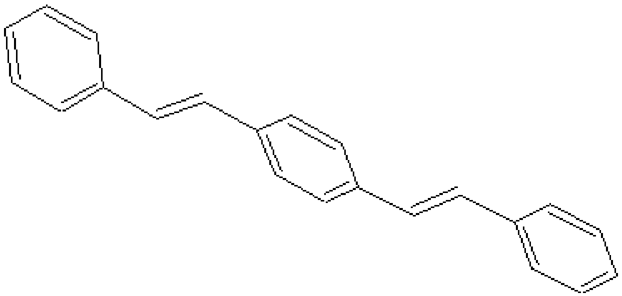
Lit.: M. Dreußen, H. Bässler, Chemie in unserer Zeit 31 (1997) 76
S. Bräse et al., Adv. Mater. 33 (2021) 2005630

10.2 Electroluminescent Molecules

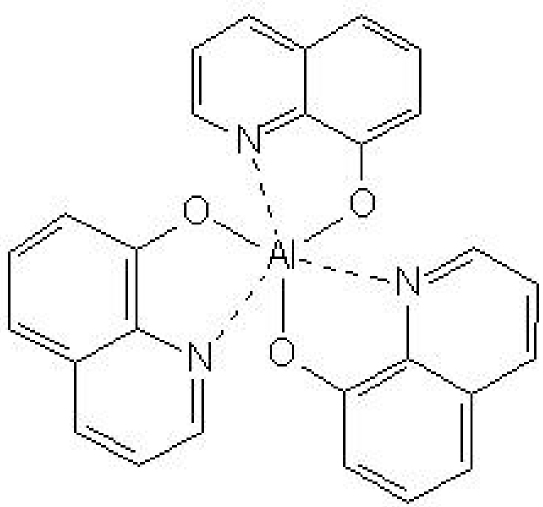
Anthracene



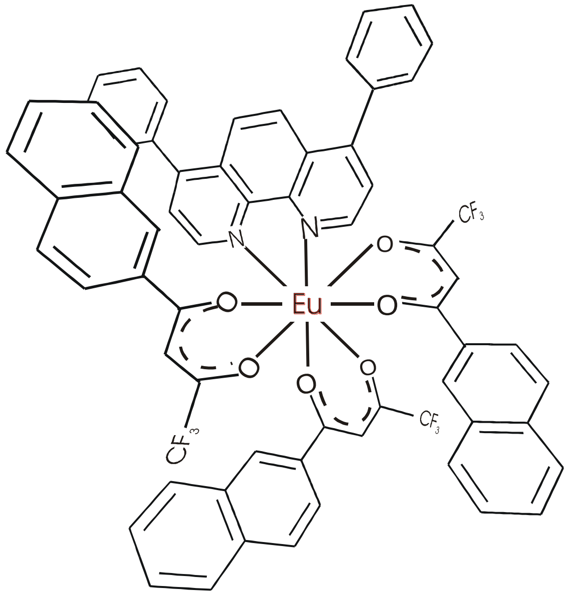
Poly-p-phenylene vinylene



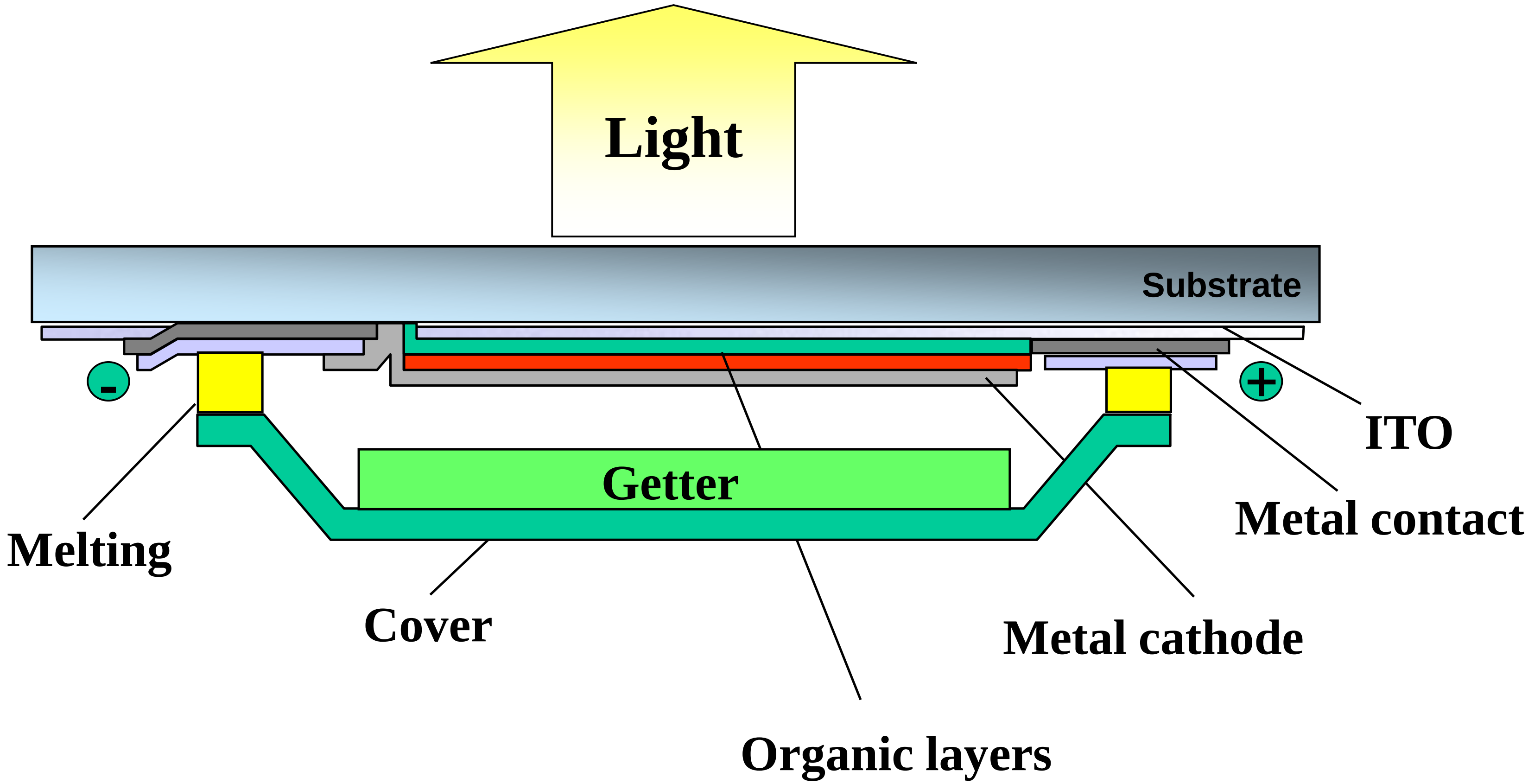
[Al(8-hydroxyquinolinate)$_3$]



Eu^{3+} complexes



10.3 Structure of OLEDs and PLEDs

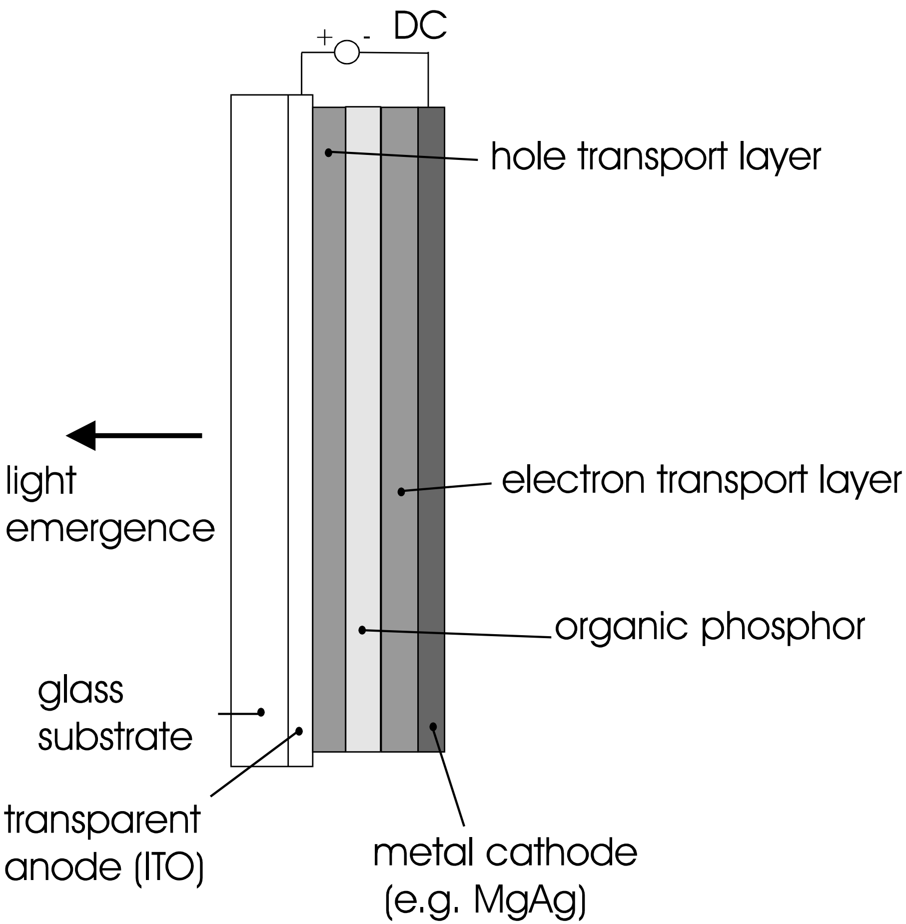


Layer preparation by

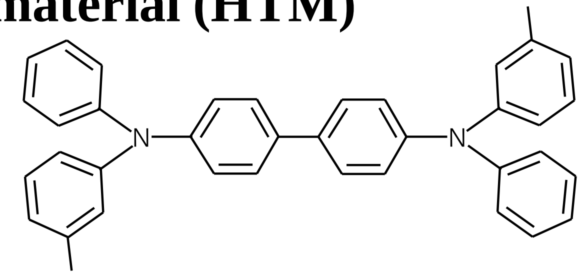
- **Vapor deposition (sublimation) of the organic components and metals**
- **Spin-coating from solutions**

10.4 Working Principle of OLEDs

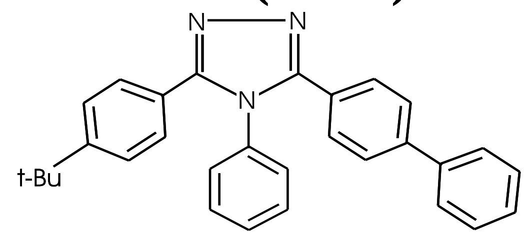
Schematic construction



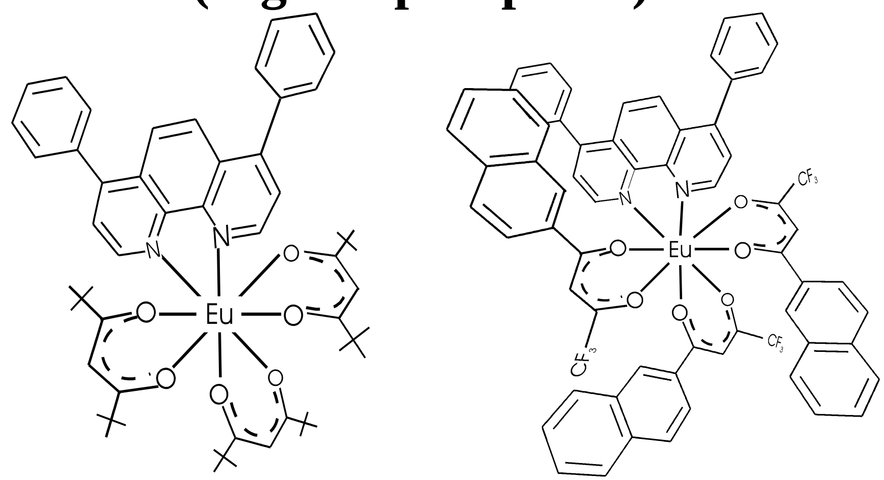
Hole transport material (HTM)



Electron transport material (ETM)

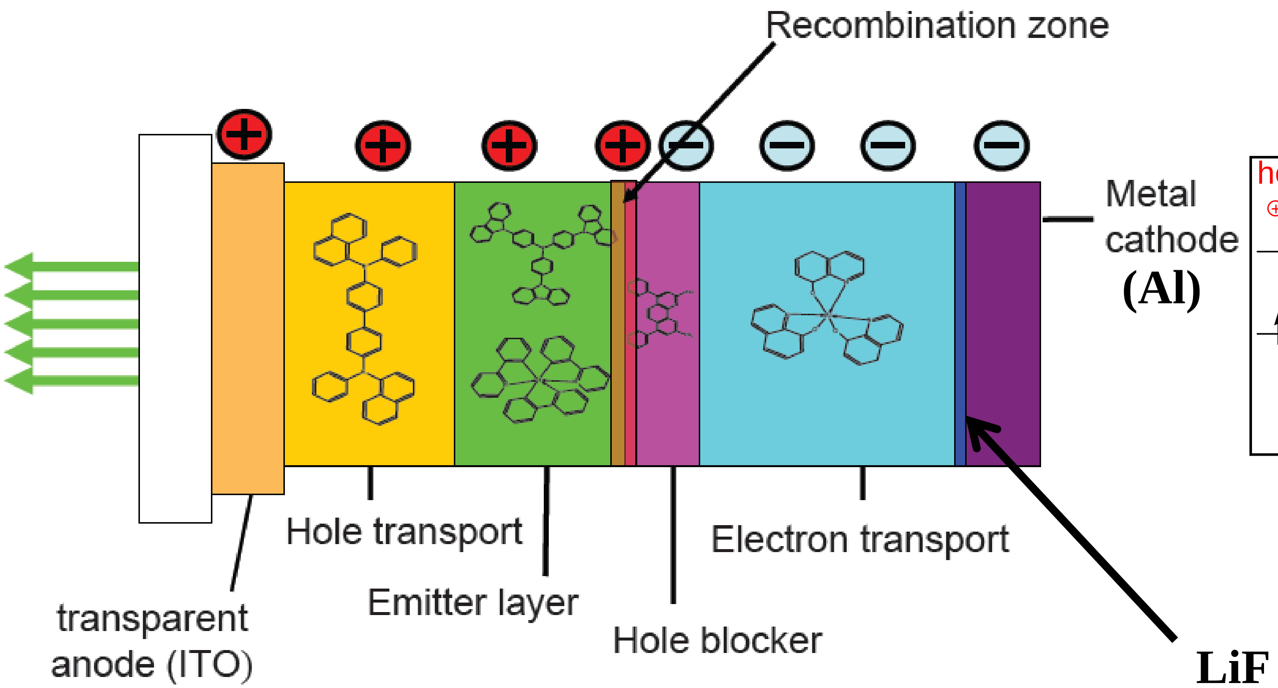


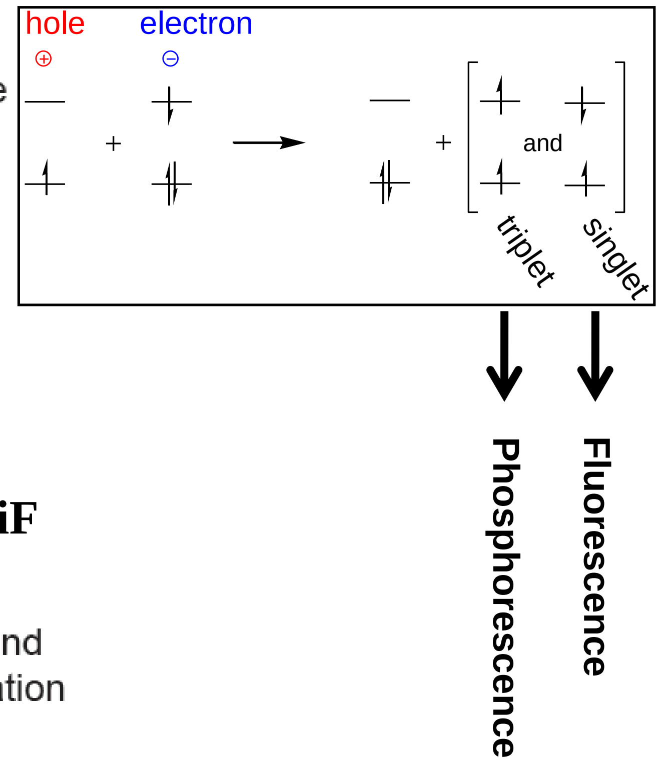
Emitter (organic phosphors)



10.4 Working Principle of OLEDs

Charge transport





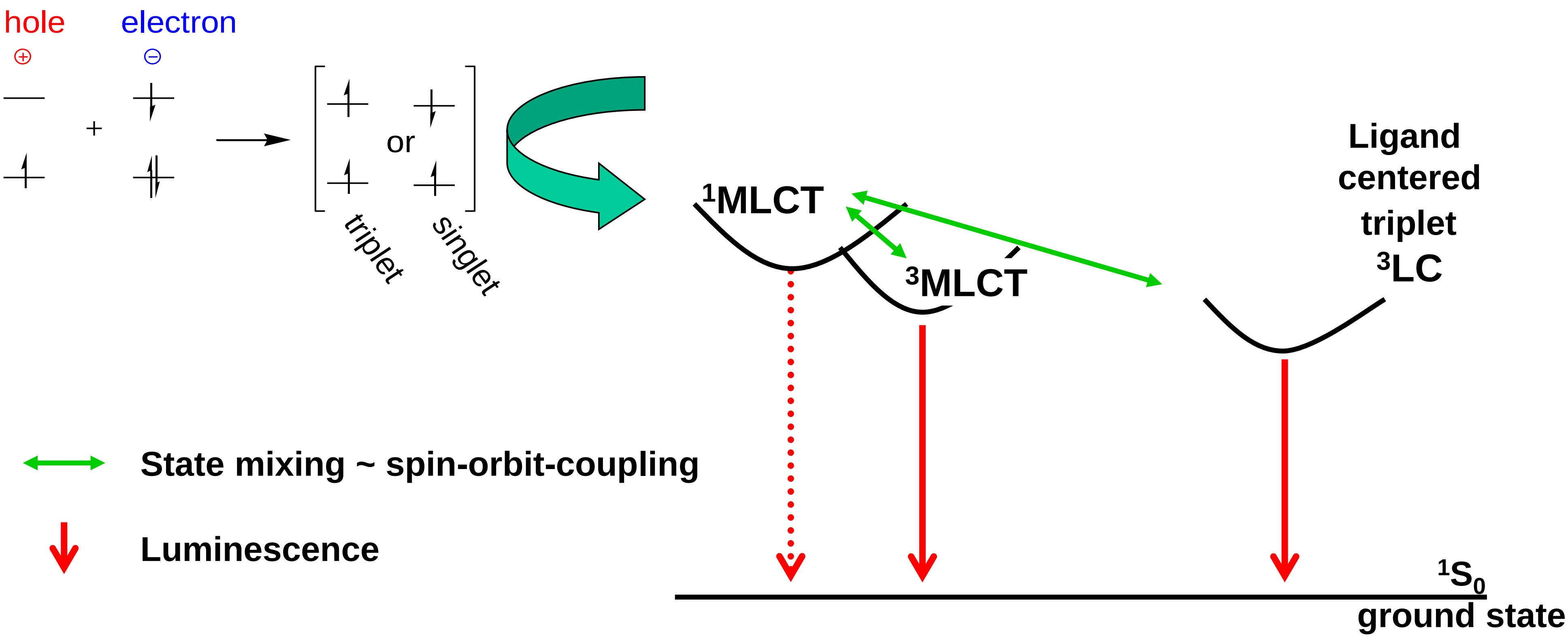
External quantum efficiency = Photon Extraction efficiency x Internal quantum efficiency x Injection and recombination

Experimentally determined singlet fraction for Alq_3 based OLEDs = 22 ± 3%

Ref.: M.A. Baldo, D. F. O’Brien, M. E. Thompson, S. R. Forrest, Phys. Rev. B 60 (1999) 14422

10.4 Physical Principle of an OLED

Energy Flow



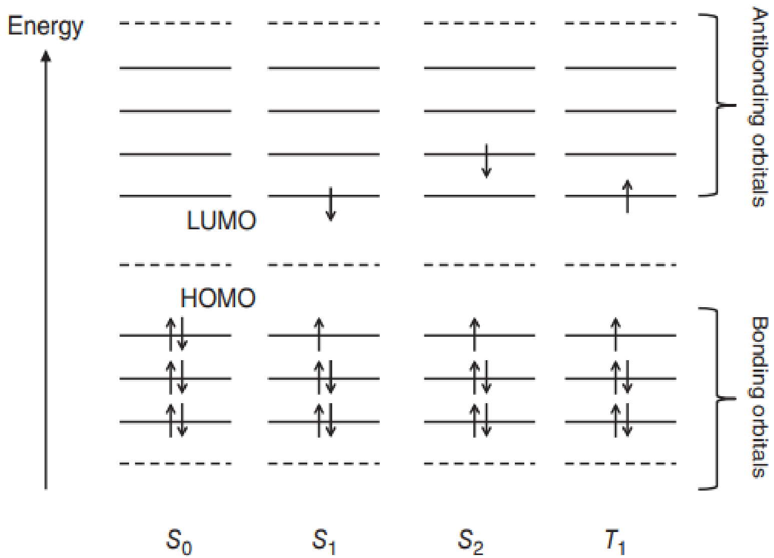
Strong spin-orbit-coupling mixes singlet and triplet MLCT states: M = Ir, Pt, Os, Re, etc.

MLCT = metal to ligand charge transfer state, LC = ligand centered state

10.4 Physical Principle of an OLED

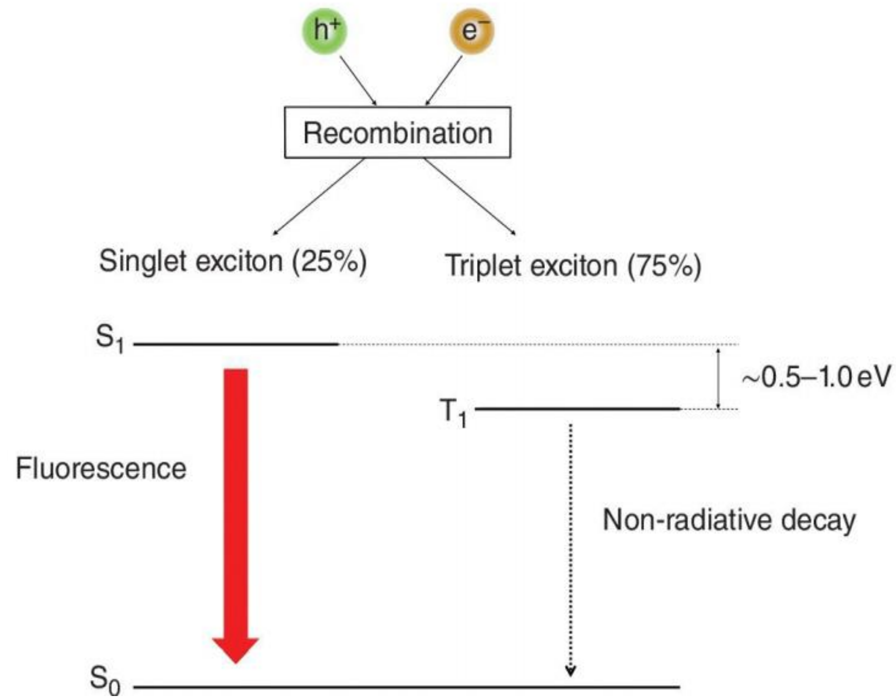
Spin Statistics

Ground and excited states



Result: 25% singlets and 75% triplets

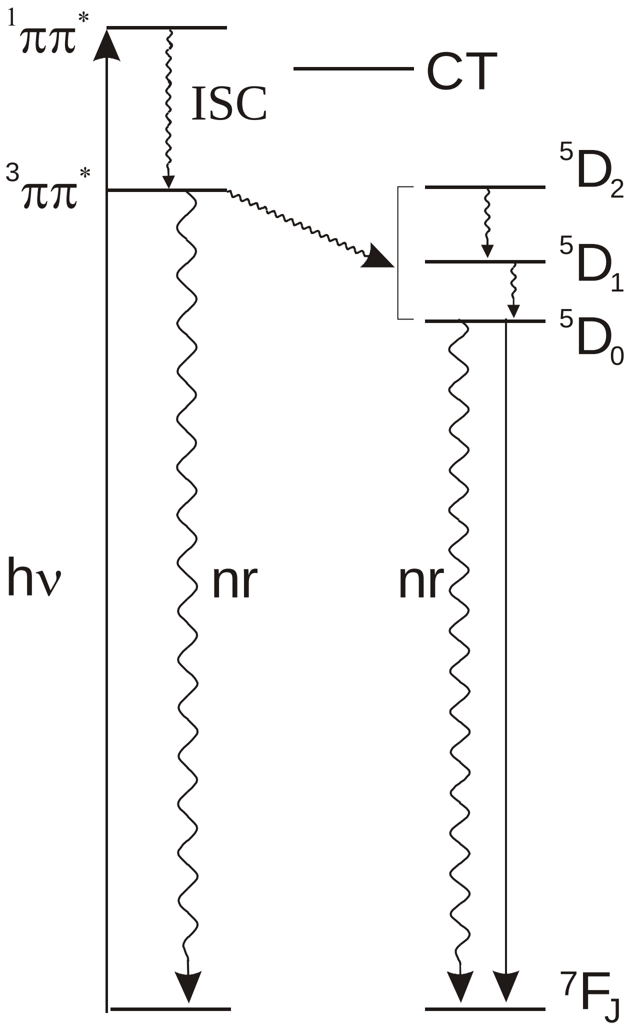
Result after exciton recombination



Challenge: Triplet harvesting to boost efficiency
by ET to metal center → Eu^{3+}
by thermally activated delayed fluorescence (TADF) → Cu^+

10.5 Luminescence of Metal Complexes

Energy level diagram of Eu^{3+}-complexes



Absorption (ligand)

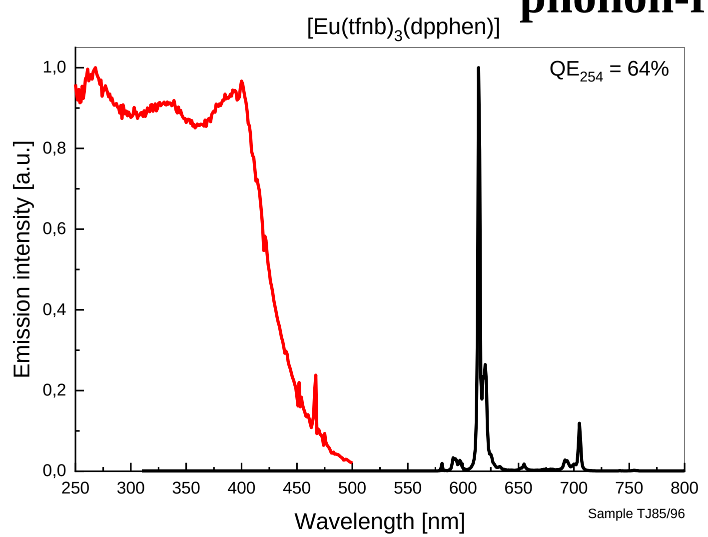
- $^1\pi-\pi \rightarrow {}^1\pi-\pi^*$
- $^1\pi-\pi^* \rightarrow {}^3\pi-\pi^*$

Ligand-metal energy transfer

- $^3\pi-\pi \rightarrow {}^5D_1, {}^5D_0$ (Eu^{3+})

Emmision (metal)

- $^5D_0$ (Eu^{3+}) $\rightarrow {}^7F_J$ (Eu^{3+})
- $^5D_1$ and $^5D_2$ levels are quenched due to electron-phonon coupling (multi-phonon-relaxation)



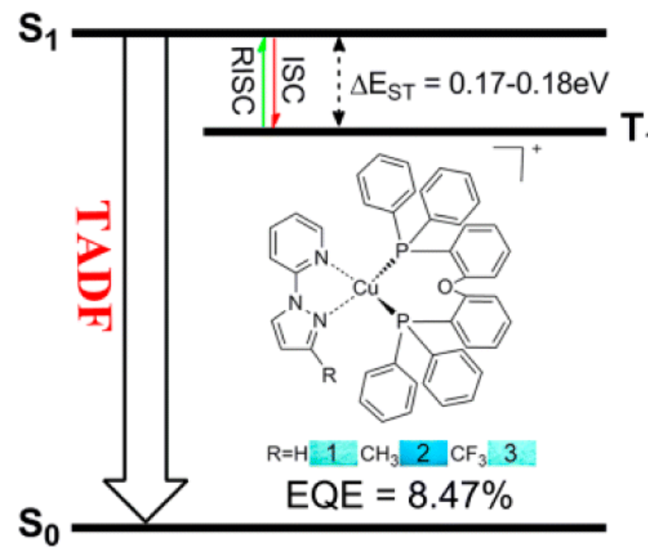
Stability of metal complexes

Thermodynamic stabilization

- High charge of metal center: 3+/4+
- Chelate or macrocyclic ligands: Porphyrin, phenanthroline, phenyl pyridine, …..

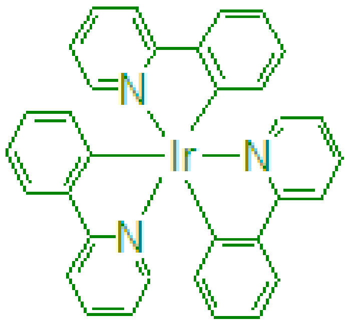
Kinetic stabilization by crystal field stabilization energy (CFSE) in octahedral (O_h) complexes

Al^{3+}	[Ne]	CFSE = 0
Cu^{+}	$[Ar]3d^{10}$	CFSE = 0
Eu^{3+}	$[Xe]4f^{6}$	CFSE ~ 0
Tb^{3+}	$[Xe]4f^{8}$	CFSE ~ 0
Re^{+}	$[Xe]4f^{14}5d^{6}$ (l.s.)	CFSE = -24 Dq_o
Ir^{3+}	$[Xe]4f^{14}5d^{6}$ (l.s.)	CFSE = -24 Dq_o
Pt^{4+}	$[Xe]4f^{14}5d^{6}$ (l.s.)	CFSE = -24 Dq_o

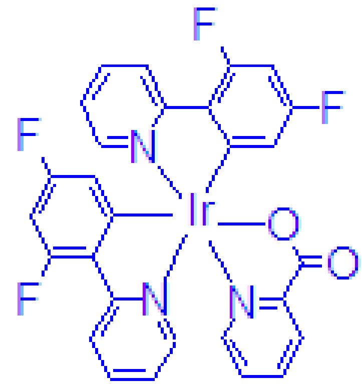


10.6 Iridium Complexes

[Ir(*ppy*)$_3$] ppy = phenylpyridine



[(4,6-F$_2$*ppy*)$_2$Ir(pic)] pic = picolinat

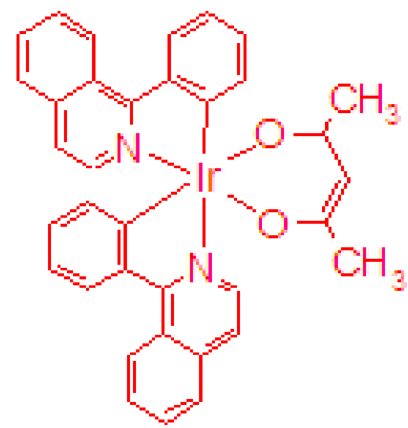


Advantages of Ir^{3+} complexes

- **Strong spin-orbit coupling ξ:**
  Ir^{3+} ~ 4000 cm^{-1}
  Compare: Mn^{4+} ~ 400 cm^{-1}

[(*pch*)$_2$Ir(acac)] pch = phenylquinolinate

acac = acetylacetonate

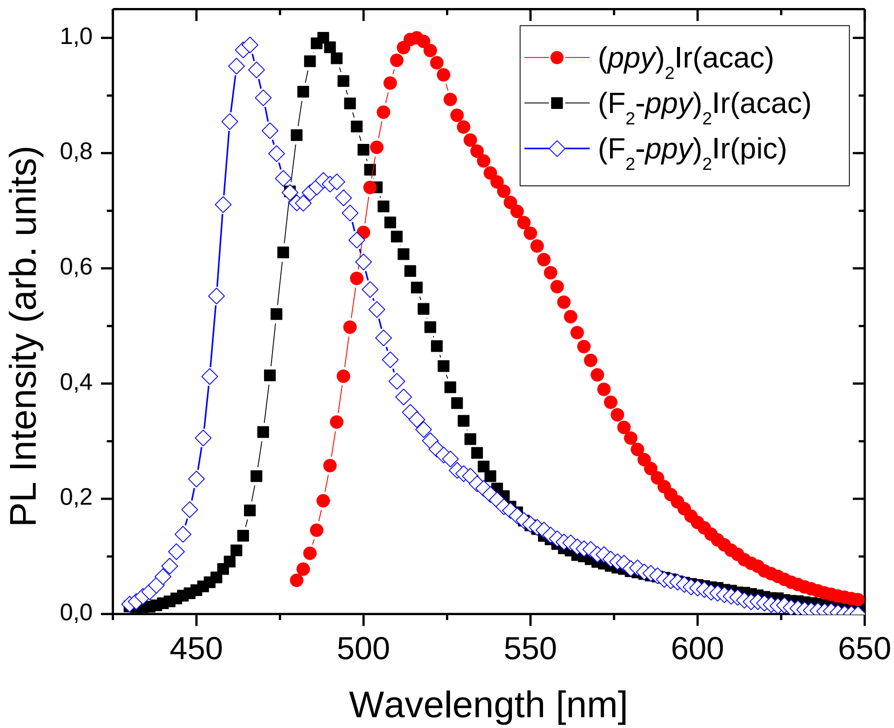


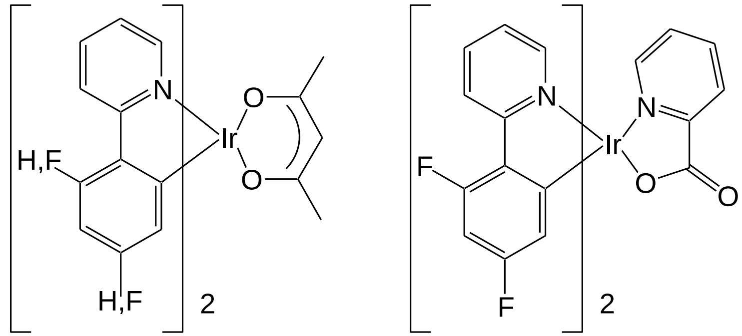
Emission spectrum of Ir^{3+} complexes

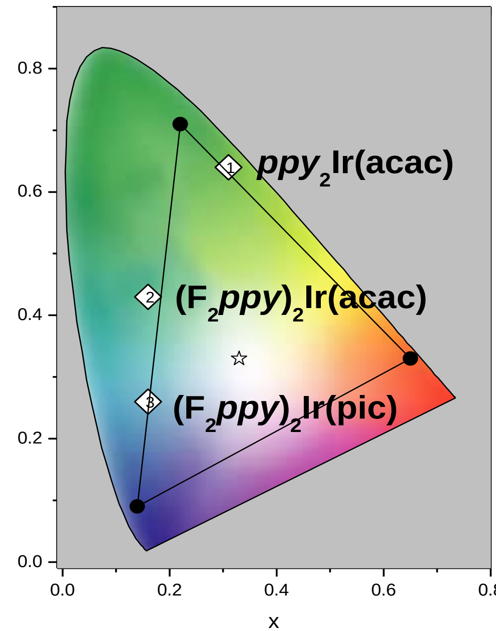
- **MLCT and $^3\pi$-π^* transitions**
- **Position of the HOMO and thus the emission bands can be determined by the ligands and controlled by substituents on the ligands**

10.6 Iridium Complexes

[(4,6-F_2-*ppy*)$_2$Ir(L)] - Photoluminescence and color points

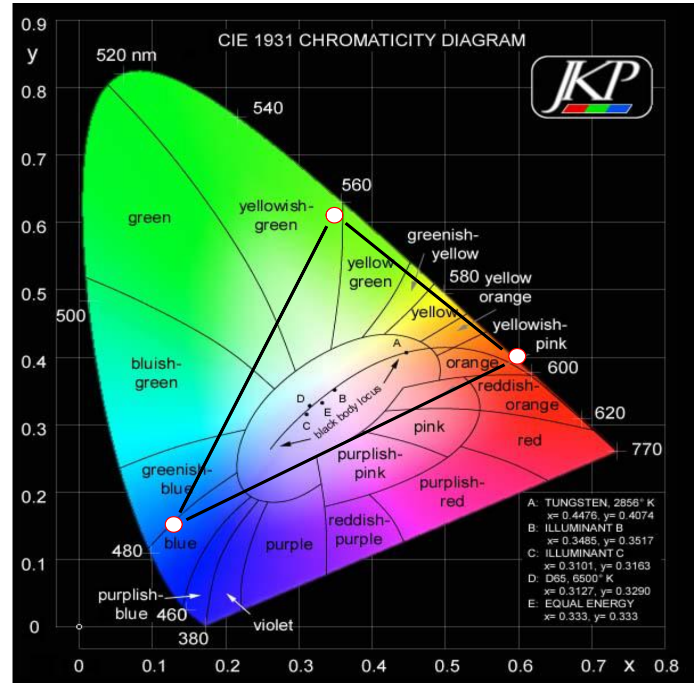






10.7 White OLEDs - Options

Emitter	Colour	Efficiency	Lifetime
Fluorescent	R	+	++
	G	+	++
	B	+	+
Phosphorescent	R	++	+
	G	++	+
	B	+	o

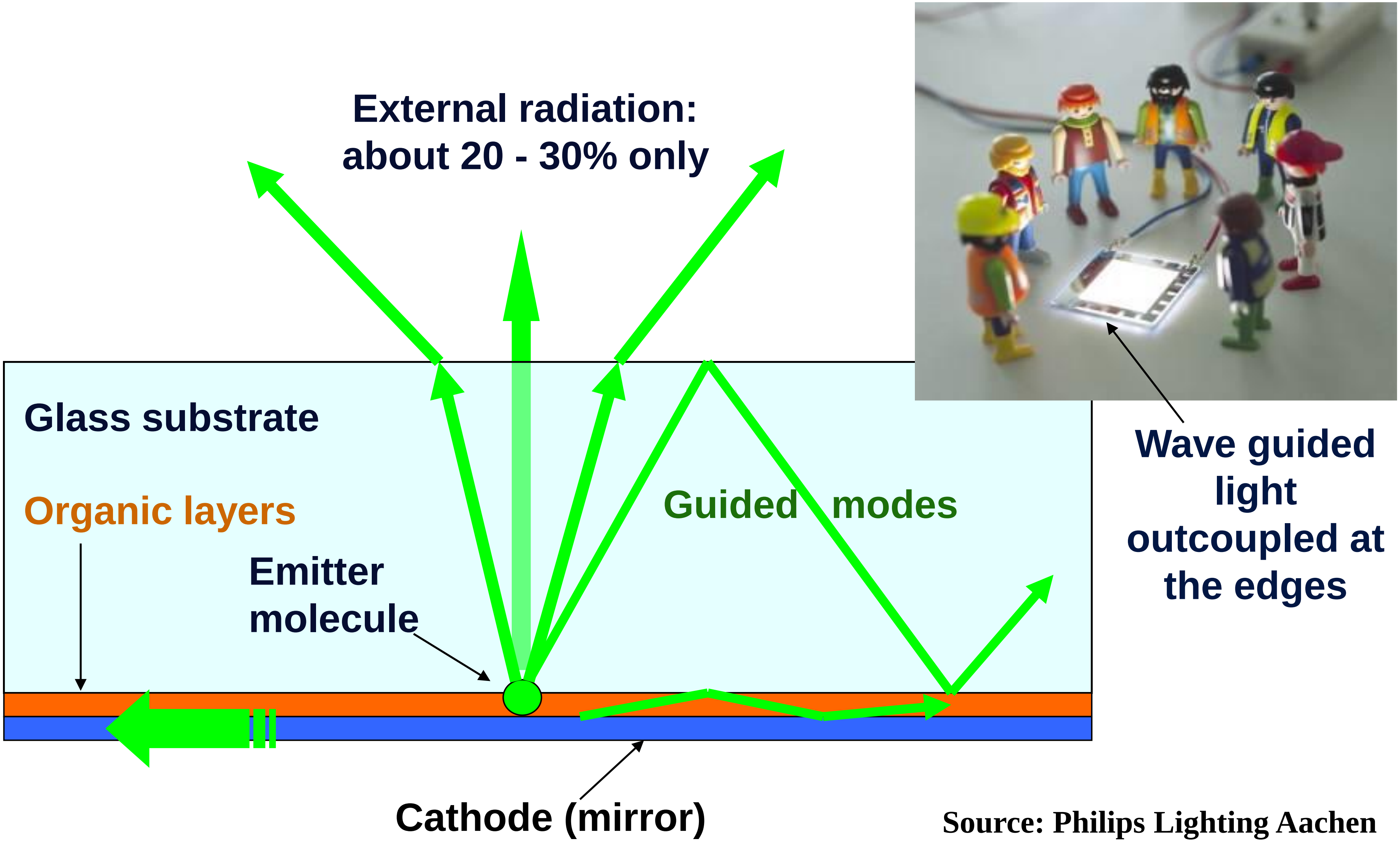


Expected external quantum efficicency without light outcoupling measures

Full fluorescent RGB	5-10%
Full phosphorescent RGB	20%
Hybrid: B fluorescent, R+G phosphorescent	16%

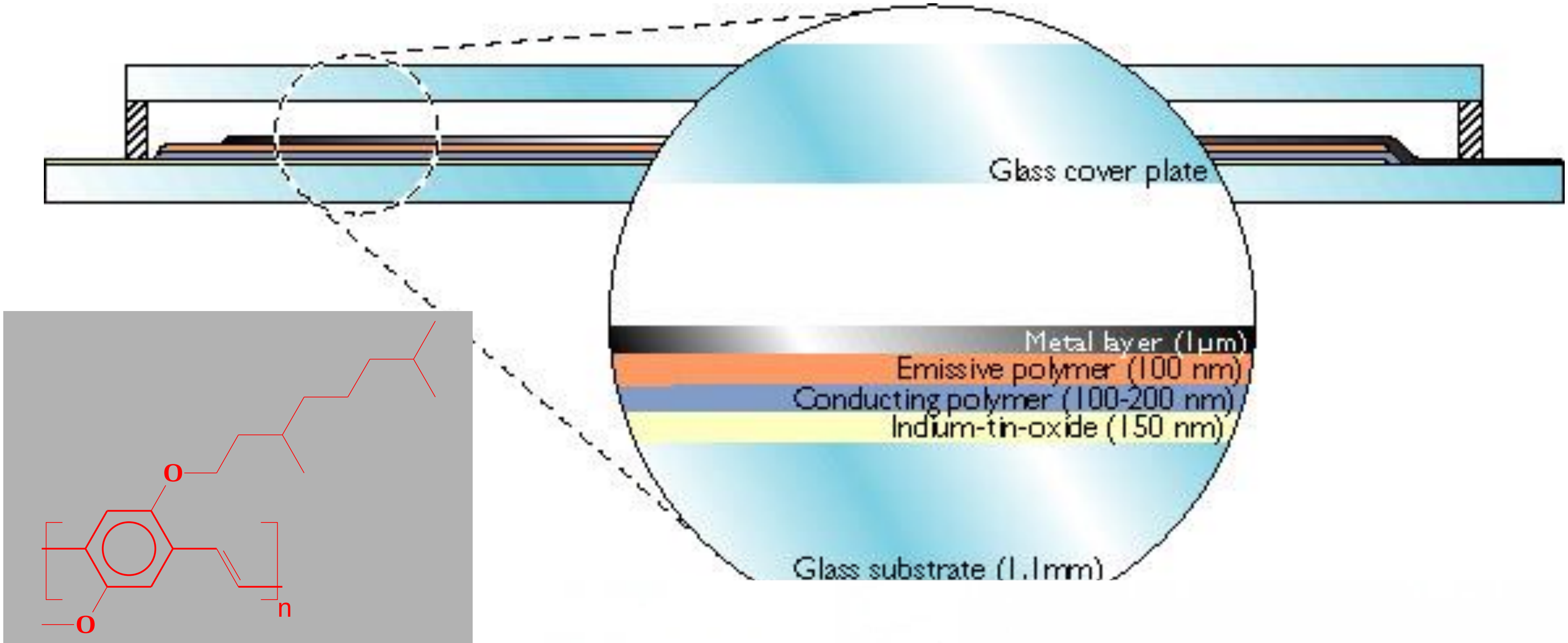
Source: Philips Lighting Aachen

10.7 White OLEDs - Light Out-coupling

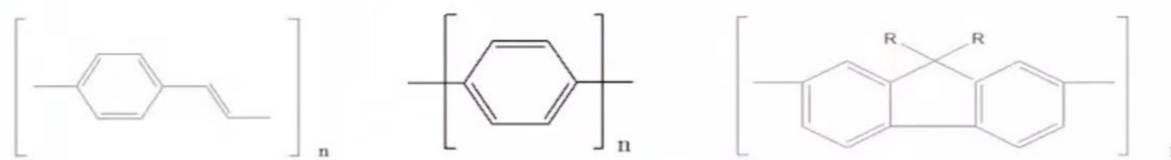


Source: Philips Lighting Aachen

10.8 Polymer LEDs - Construction



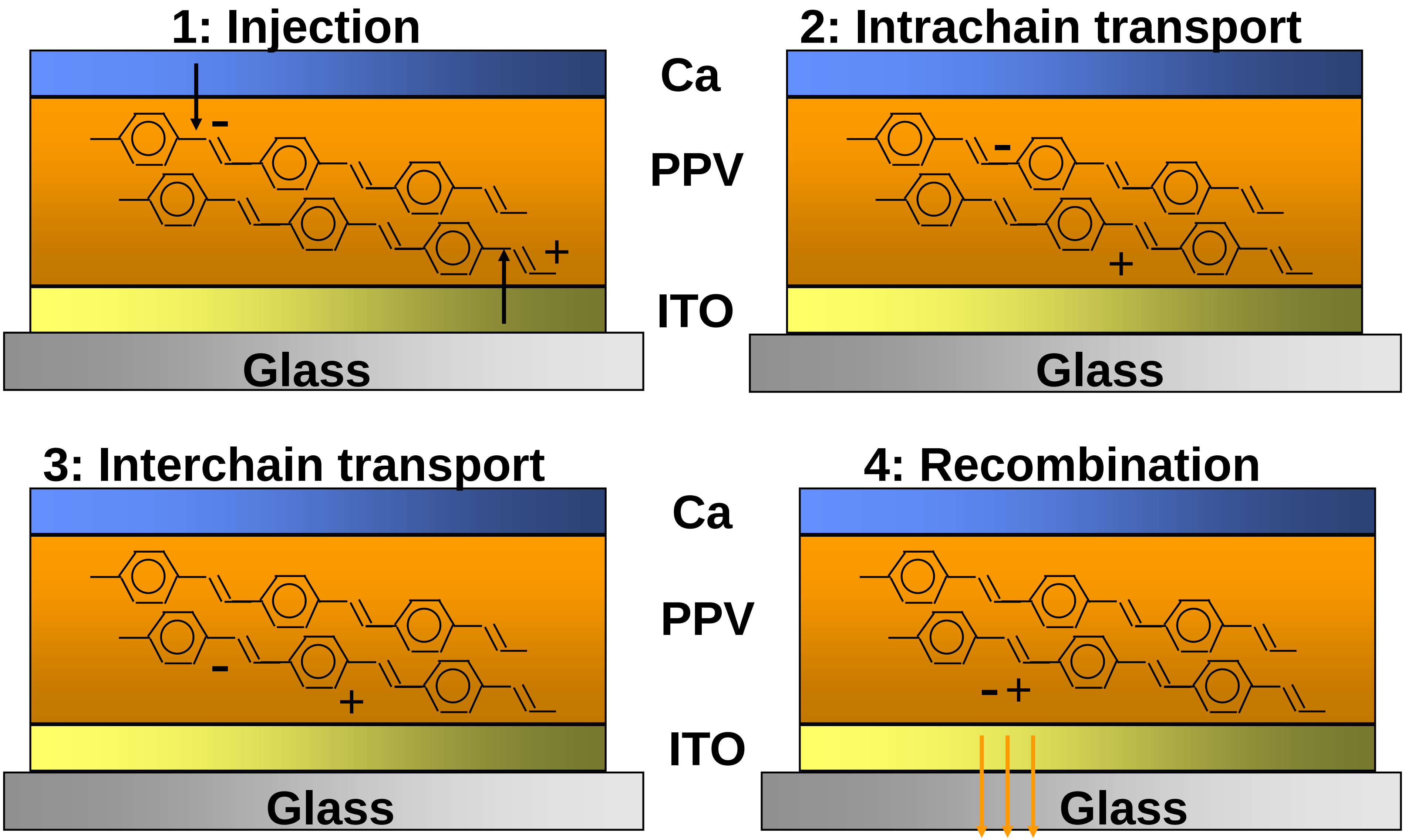
Poly(dialkoxy-p-phenylenevinylene) “PPV”



Poly(p-phenylene vinylene) Polyphenylene Poly(9,9' dialkyl fluorene)

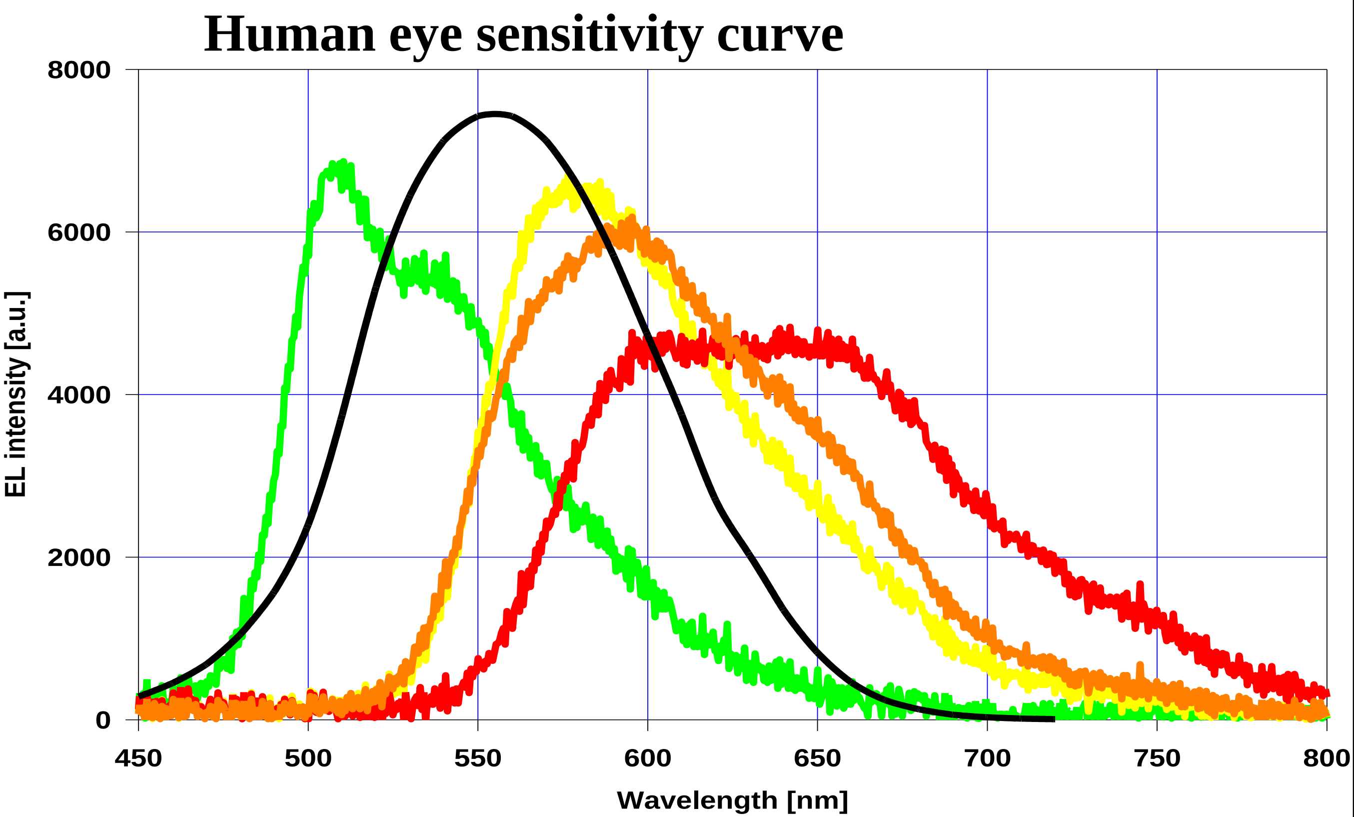
Source: Philips Lighting Aachen

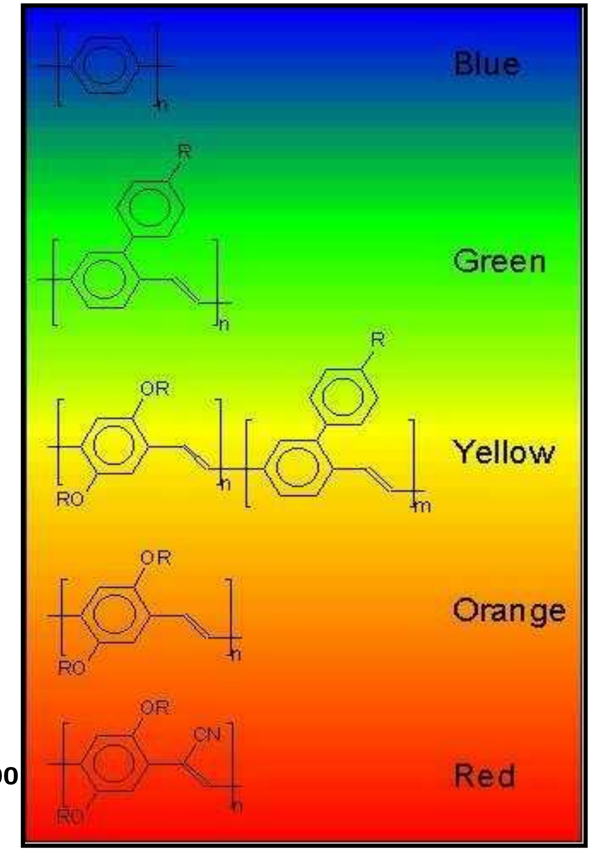
10.9 Operation of a Polymer LED



10.10 Polymer LED Spectra

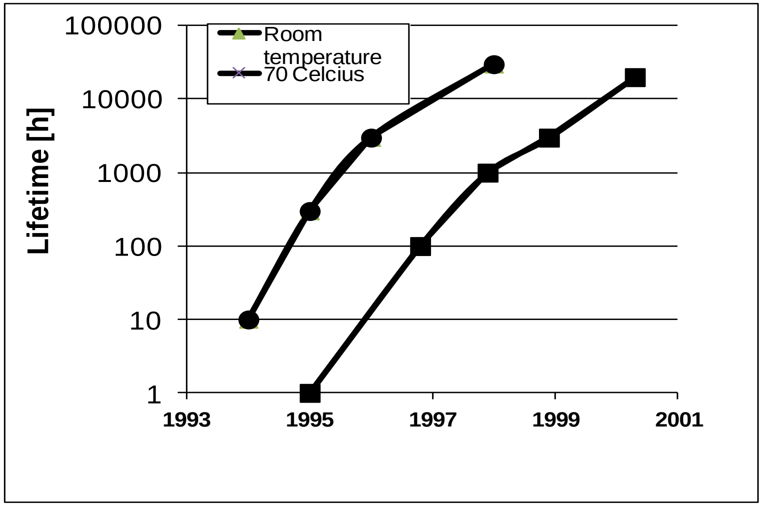
Emission spectra of some polymers





Source: Philips Lighting Aachen

10.11 Development of Lifetime, EQE & Luminance

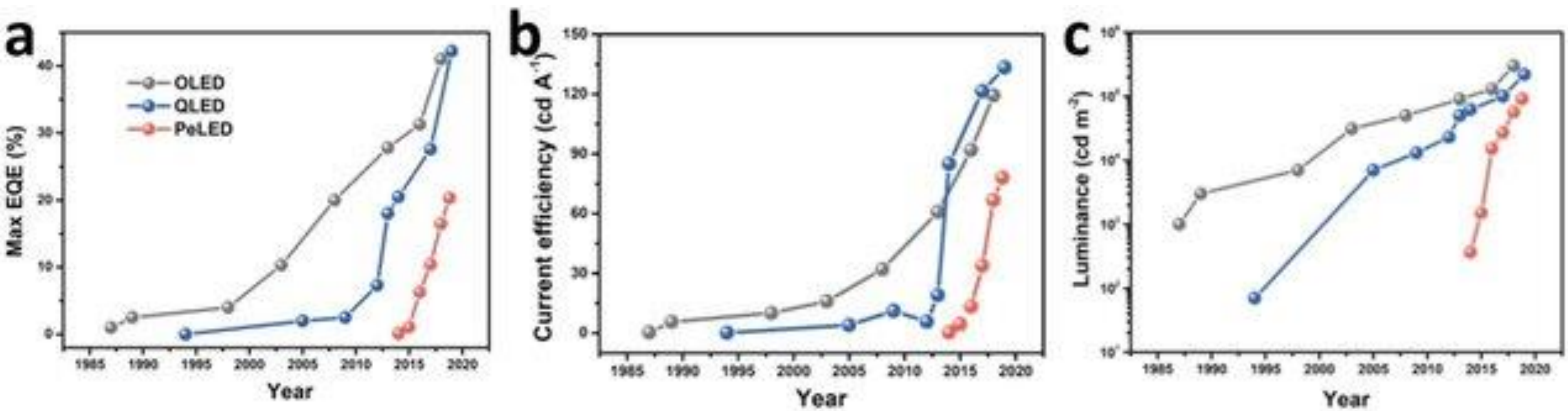


In the beginning (Y1994-2001):

Temperature is an issue!

100 kh lifetime is in reach, but dependent on drive

(Data for 20 cd/m^2 brightness)

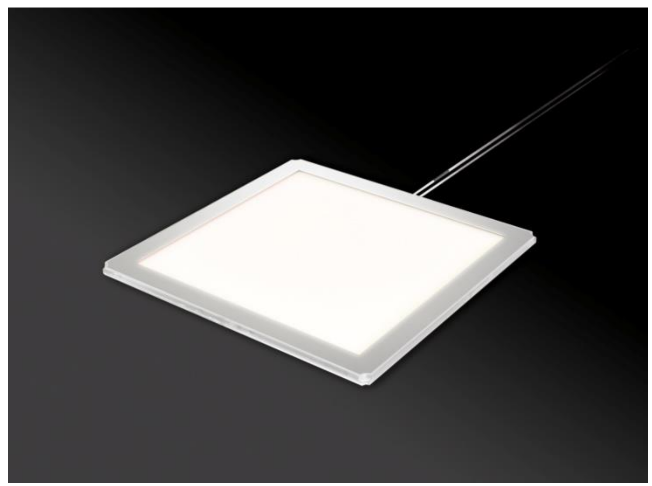


Degradation due to O_2 and H_2O $\Rightarrow$ Encapsulation and getter are required

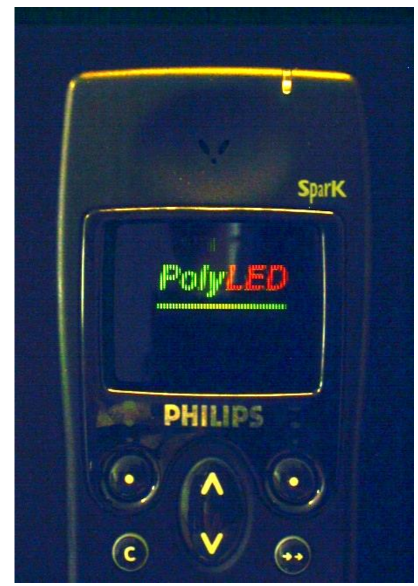
10.12 Application Areas

Flexible displays without backlight and superior contrast

- Shaver displays
- Digital cameras
- Warning signs
- OLED TVsets/displays
- Light tiles
- Smart phones
- Indoor illumination



Philips Lumiblade

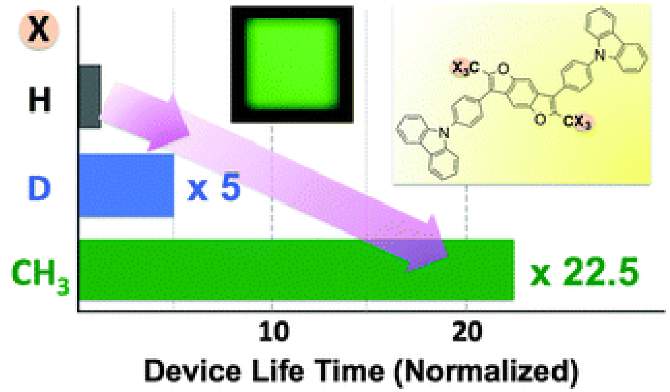


10.13 Future Developments

Novel materials and novel applications

• **Deuterated, methylated HTM, ETM, and emitter materials to enhance device lifetime**
Ref.: H. Tsuij et al., Chem. Comm. 50 (2014) 14870

Deuteration by high-pressure treatment in D_2O vapor $\rightarrow$ up to ~75%



• **Organic Photovoltaic (OPV)**
Efficiency 2023: 19.2%
Ref.: J. Hou et al., Adv. Mater. (2023) 2301583