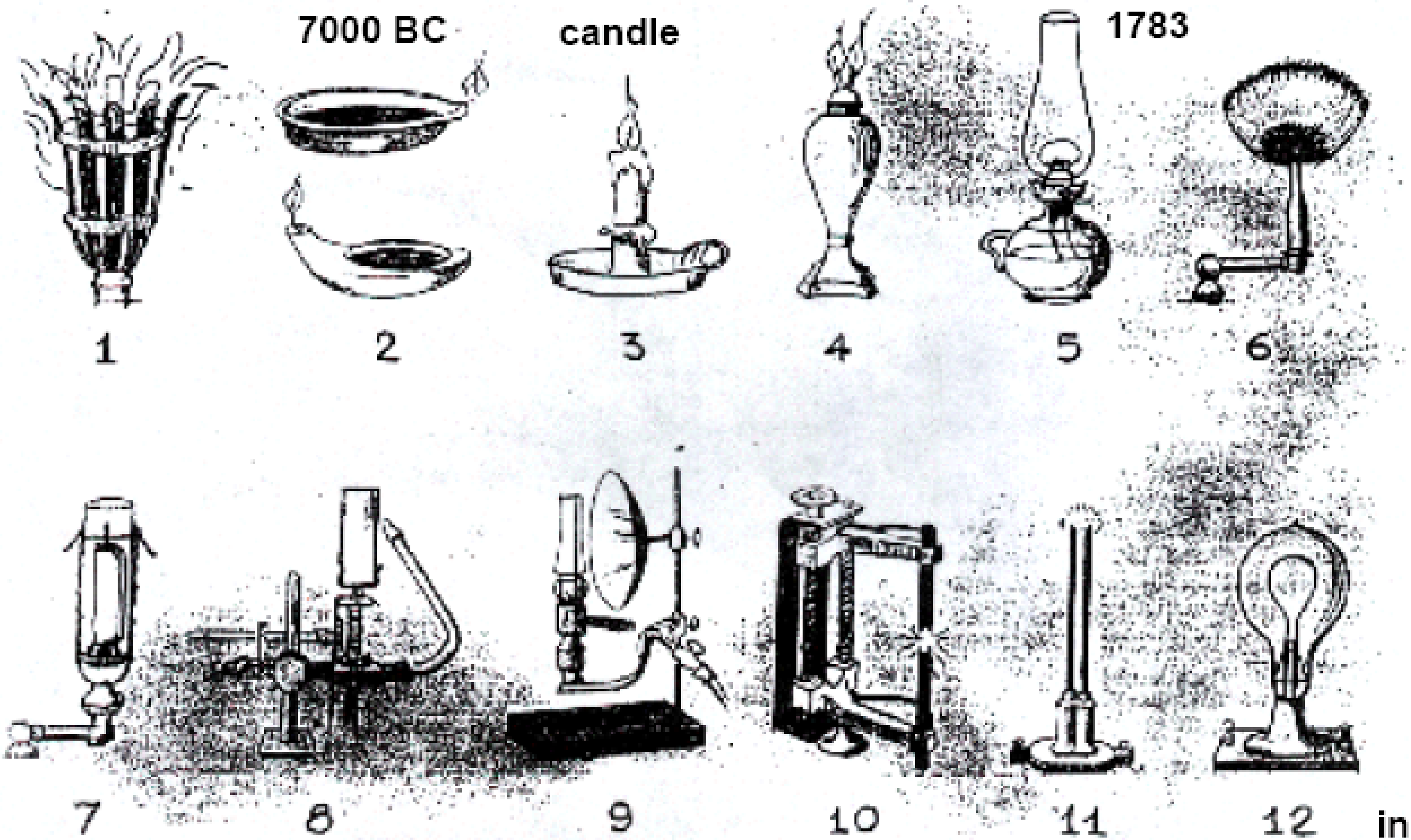
Organic light-emitting devices (OLEDs)

A short history of lighting devices



lifetime (45 h)
efficiency 1.4 lm/W.

About 20 % of electricity in the world is consumed for lighting

(Switzerland: 10 % of household electricity, 2% of total national electricity)

Commercial sources

(fading out)

72 W	14 W	100 W	23W
5000 h	30 000 h	1000 h	10000 h
20 lm/W	100 lm/W	15 lm/W	60 lm/W to 80 lm/W (tube)

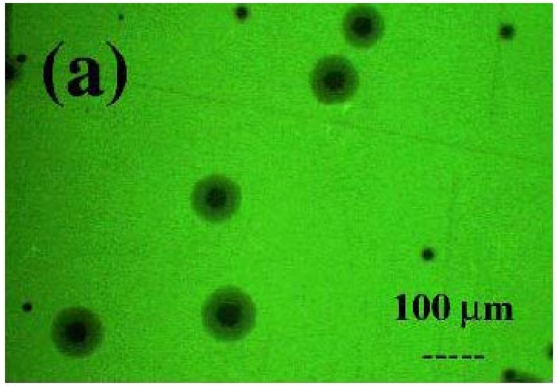
OLED Displays

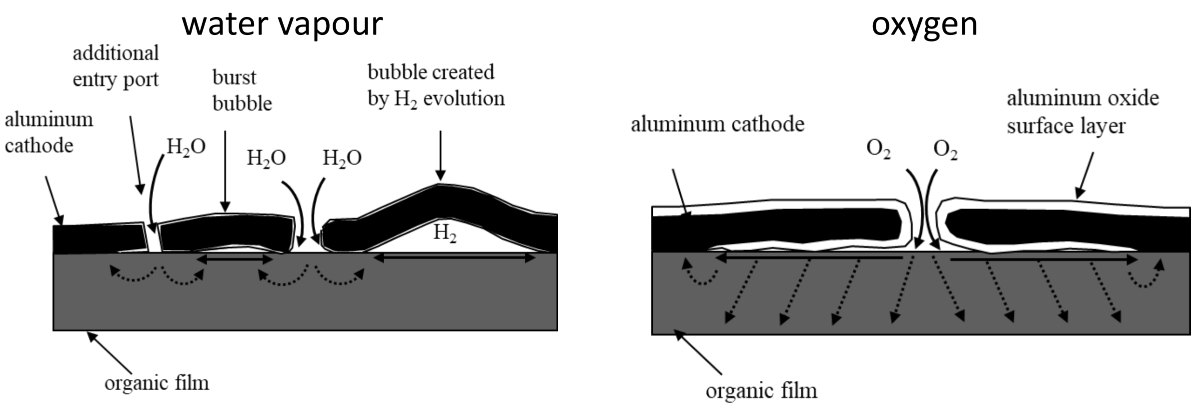
(15% of the display market share, 65% of the smartphone display market share in 2021)

The importance of encapsulation

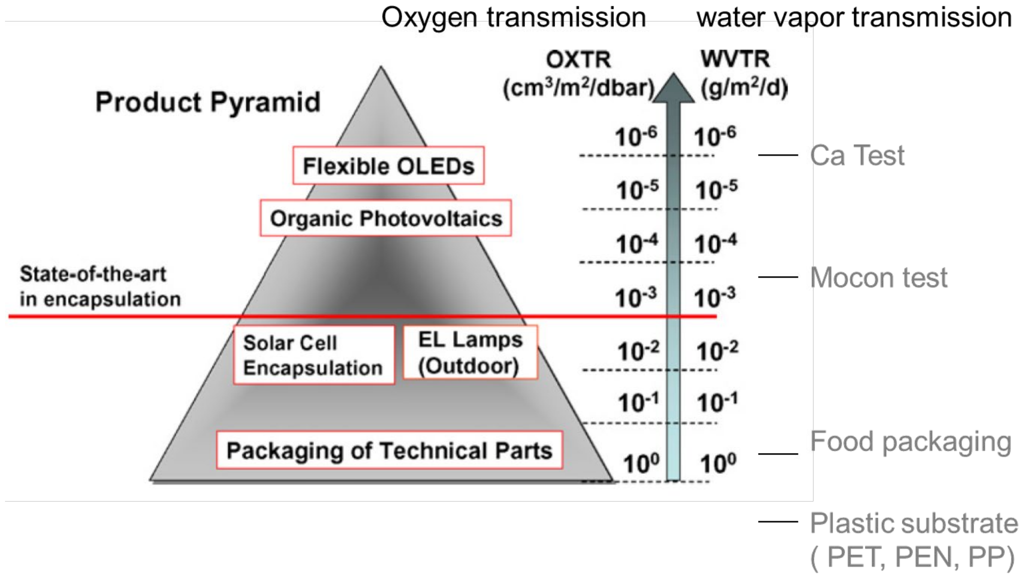
⇒ Oxide formation at cathode/organic interface
⇒ Electrode delamination (gas pressure)
⇒ Photo-oxidation => quenching

dark spot formation



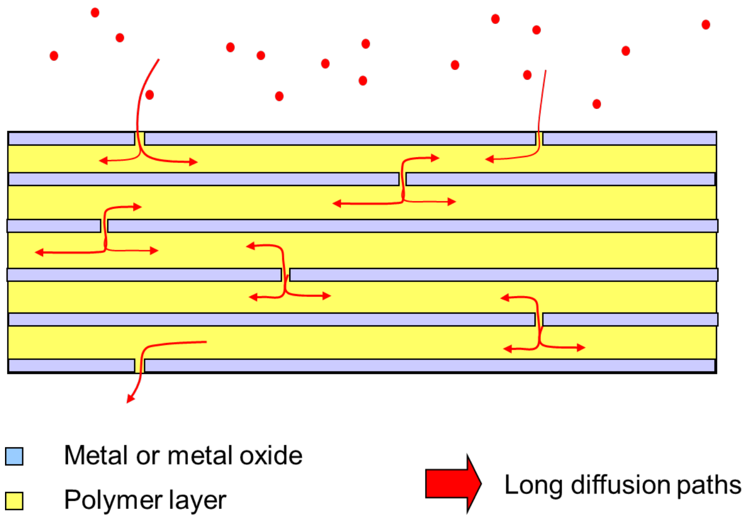


M. Schaer, F. Nüesch, D. Berner, W. Leo, L. Zuppiroli, *Adv. Func. Mater.*, 11 (2), (2001), p.116-121.



S. Logothetidis *Materials Science and Engineering B* 152 (2008) 96–104

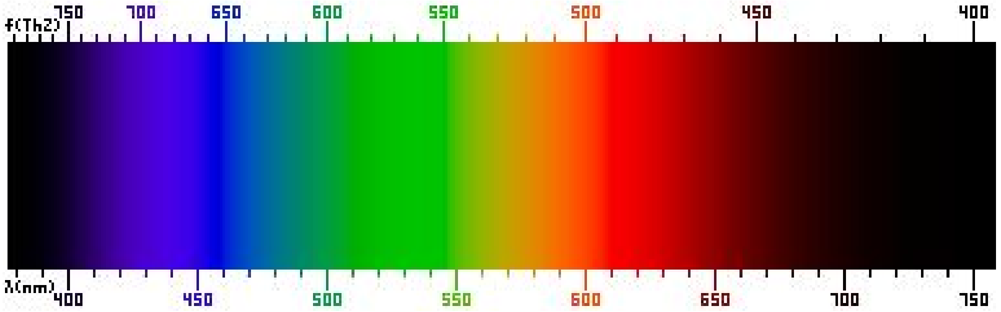
Basic strategy for flexible barrier foils:



Units and color coordinates used for emissive devices

Radiometry is the measurement of radiation in the electromagnetic spectrum. This includes ultraviolet (UV), visible and infrared (IR) light. Electromagnetic radiation is characterized by its frequency of oscillation ν, which is related to the wavelength λ by the speed of light c:

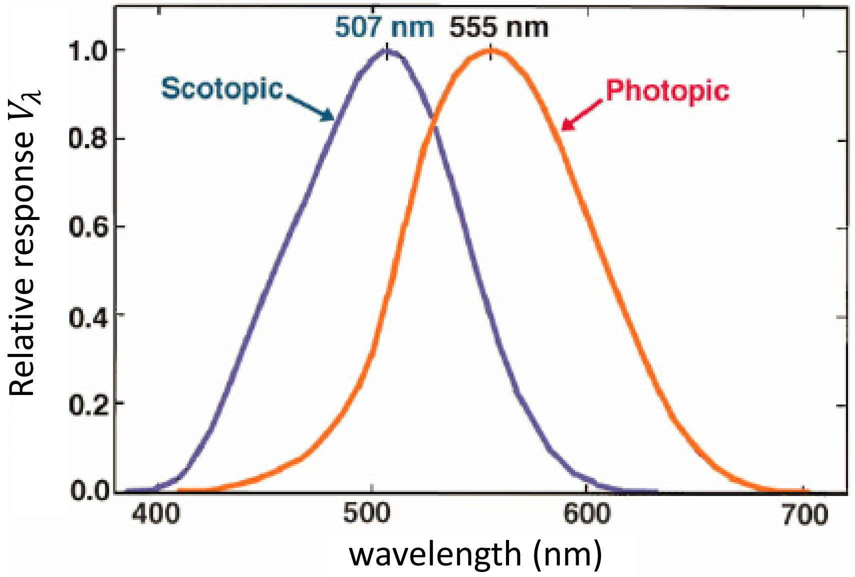
$$\nu = \frac{c}{\lambda}$$



Radiometric units are based on SI units (W, J etc.) and are the preferred unit in optics. For lighting devices however we need to include the user and the response of the eye.

Photometric units

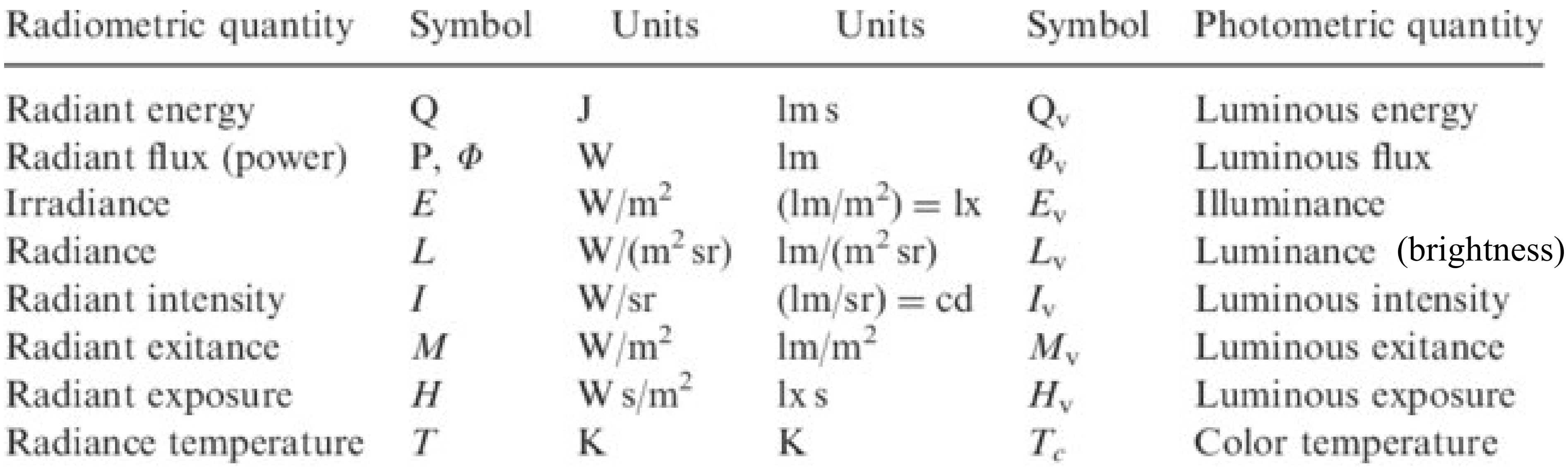
The human eye has a specific spectral response which also depends on the intensity. Those are called the photopic (day vision) and scotopic (night vision) responses: Blue light will be perceived as much dimmer as green light of the same intensity (in Watts). These curves were obtained by averaging the light intensity felt by the observer over a very large group of persons. As can be seen from the photopic curve, our eye is most sensitive to 555 nm photons (green).



Having defined the eye’s spectral response, the Commission Internationale de l’Eclairage (CIE) sought a standard light source to serve as yardstick for luminous intensity. The first source was a specific type of candle, giving rise to the terms foot-candle and candlepower. In an effort to improve repeatability, the standard was redefined in 1948 as the amount of light emitted from a given quantity of melting platinum. The basic unit of photometry is the lumen (lm), which is related to its radiometric analogue, the Watt, by:

$$\phi_\lambda[lm] = 683\left[{}^{lm}/_{W}\right] I_\lambda\,[W]\,V_\lambda$$

V_λ is the relative luminous response of the human eye and I_λ is the radiant flux.



Radiometric quantity	Symbol	Units	Units	Symbol	Photometric quantity
Radiant energy	Q	J	lm s	Q_v	Luminous energy
Radiant flux (power)	P, Φ	W	lm	Φ_v	Luminous flux
Irradiance	E	W/m^2	(lm/m^2) = lx	E_v	Illuminance
Radiance	L	W/(m^2 sr)	lm/(m^2 sr)	L_v	Luminance (brightness)
Radiant intensity	I	W/sr	(lm/sr) = cd	I_v	Luminous intensity
Radiant exitance	M	W/m^2	lm/m^2	M_v	Luminous exitance
Radiant exposure	H	W s/m^2	lx s	H_v	Luminous exposure
Radiance temperature	T	K	K	T_c	Color temperature

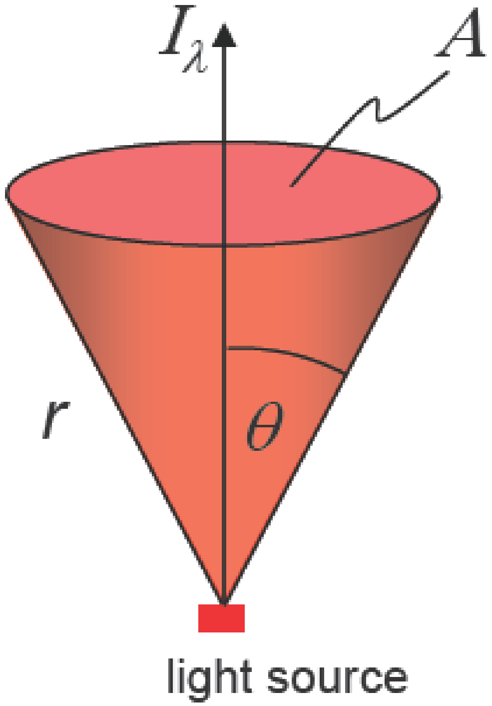
Besides the lumen, the most widely used photometric unit is the candela, defined as luminous intensity (in candela). **Brightness (or luminance)** is given in candela/m^2. Candela (cd) are lumen/steradian (lm/sr) and are related by the following formula:

$$I_\lambda^{cand}[cd\ or\ lm/sr] = 683\left[{}^{lm}/_{W}\right] I_\lambda^{W}\left[{}^{W}/_{sr}\right] V_\lambda$$

Photometric power emitted by a source

For an isotropic emitter the luminous flux emitted into half space can by easily obtained from the luminous intensity I_λ^W in forward direction and multiplying by the solid angle Ω :

$$\Omega = \frac{A}{r^2} = 2\pi(1-\cos\theta)$$

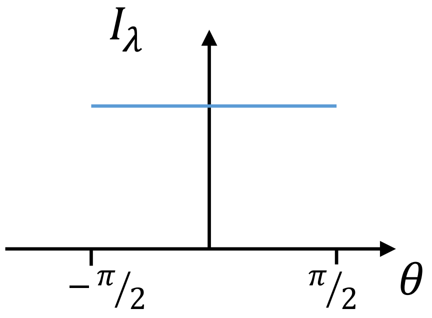


For half space, the solid angle corresponds to 2π and therefore $\phi_\lambda[lm] = I_\lambda^{cand} 2\pi$ for the isotropic emitter.

It is a bit more complicated for other emitters such as the Lambertian emitter where $I_\lambda^{cand}(\theta) = I_\lambda^{cand}(0)cos\theta$. In the latter case one can show that $\phi_\lambda[lm] = I_\lambda^{cand}(0)\,\pi$.

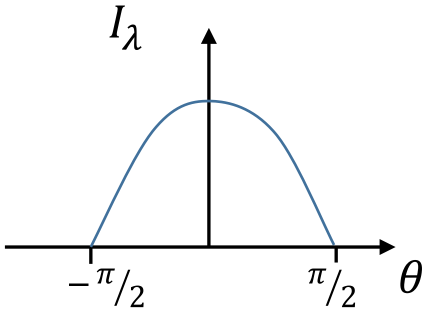
Isotropic emitter (half space)

$$\phi_\lambda[lm] = I_\lambda^{cand}(0)\,2\pi$$



Lambertian emitter (half space)

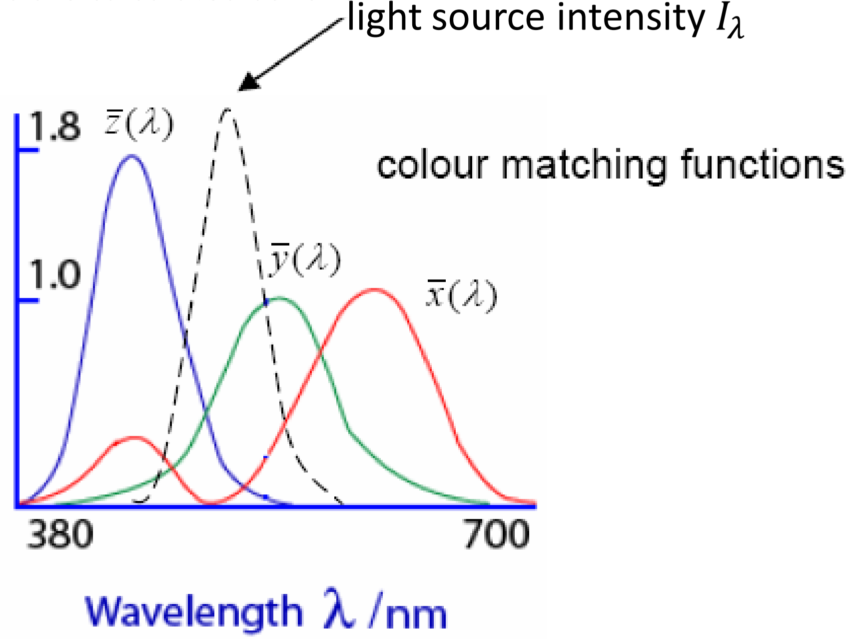
$$\phi_\lambda[lm] = I_\lambda^{cand}(0)\,\pi$$



Color coordinates

The perception of colour by the human eye is difficult to quantify by simply taking the emission spectrum of a given light source. Based on psycho-physical measurements, colour matching functions $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ have been adopted by the CIE (Commission Internationalede l' Eclairage) to simulate the three "pigments" present in the human retina. For an arbitrary homogeneous light source that has a given intensity as a function of wavelength (colour) given by I_λ, the three responses *X, Y, Z* called the tristimulus values are calculated as follows:

$$X = \int_0^\infty I(\lambda)\bar{x}(\lambda)d\lambda \qquad Y = \int_0^\infty I(\lambda)\bar{y}(\lambda)d\lambda \qquad Z = \int_0^\infty I(\lambda)\bar{z}(\lambda)d\lambda$$



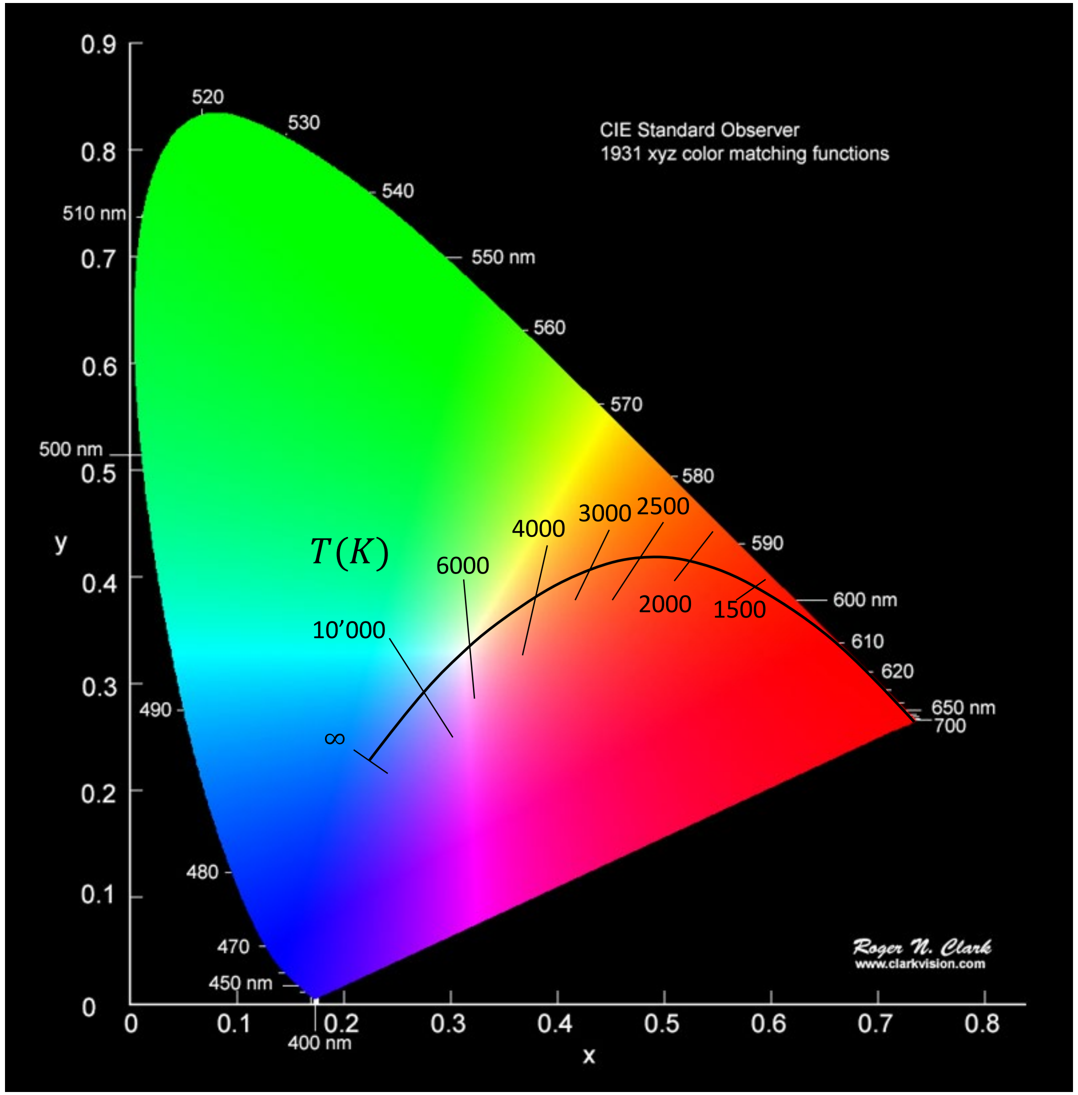
Based on these functions, the chromaticity coordinates which reflect the perceived colour are defined as normalized values:

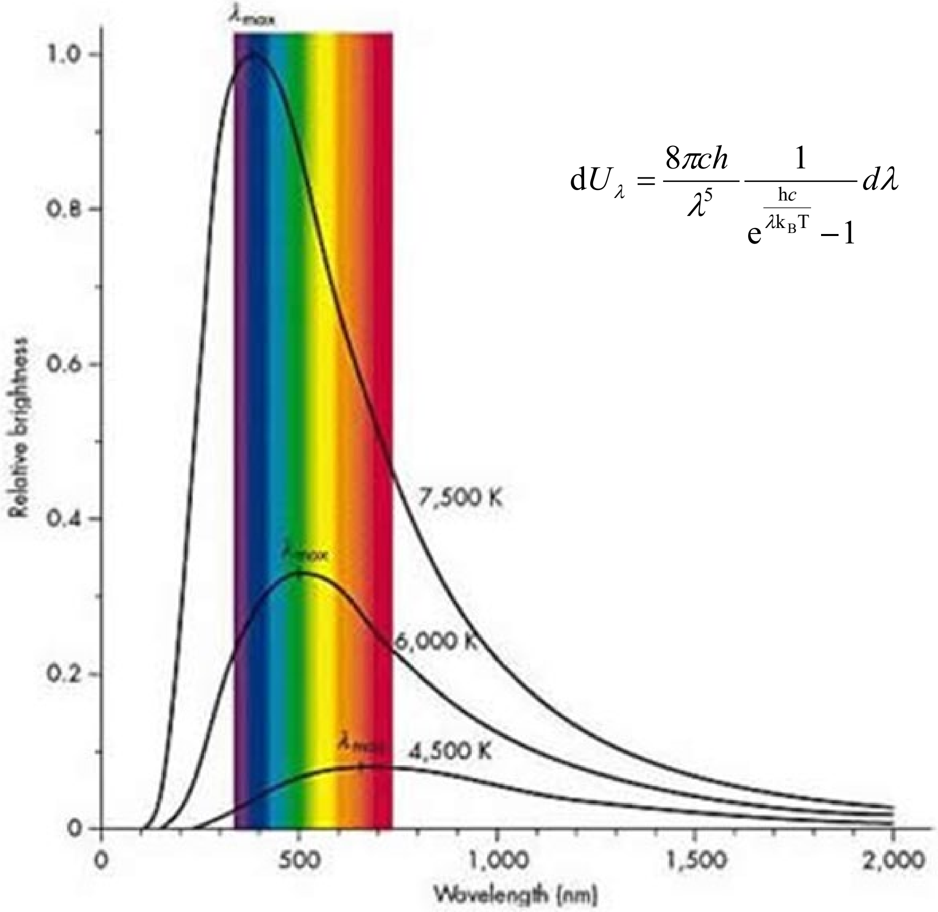
$$x = \frac{X}{X+Y+Z} \qquad y = \frac{Y}{X+Y+Z} \qquad z = \frac{Z}{X+Y+Z}$$

Therefore only two coordinats are required to indicate the color since $x + y + z = 1$.

Publication CIE No 15.2 (1986). Central Bureau of the CIE, A-1033 Vienna, P.O.Box169, Austria.

Color temperature

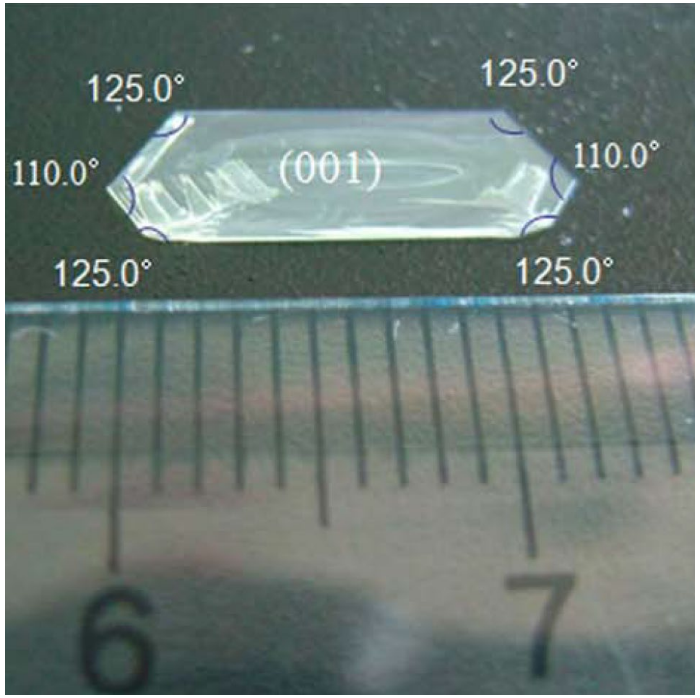


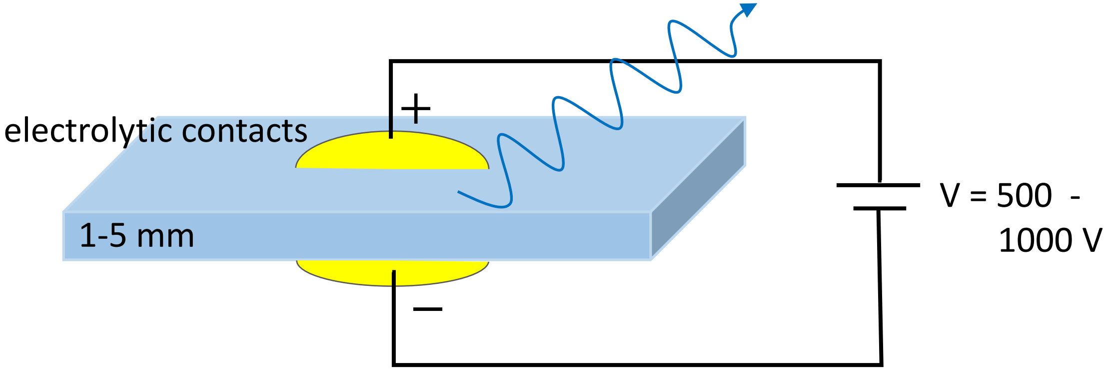


$$dU_\lambda = \frac{8\pi ch}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_B T}}-1}d\lambda$$

It is interesting to note that the chromaticity diagram not only permits to analyze colour of an emitter, but also permits to synthesize new colours. For example by using a mixture of two colours it is possible to generate new colours along the line connecting their respective coordinates.

OLED device milestones




electrolytic contacts

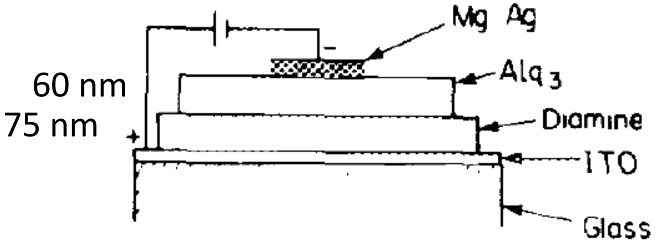
+

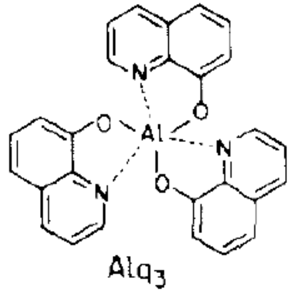
1-5 mm

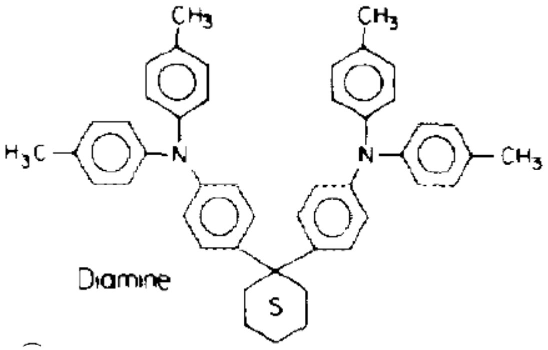
−

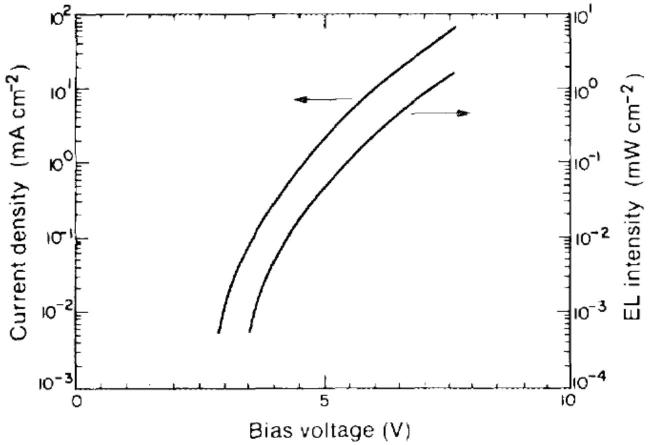
V = 500 - 1000 V

W. Helfrich, W. G. Schneider, Phys. Rev. Lett., 14, 229 (1965)


60 nm
75 nm



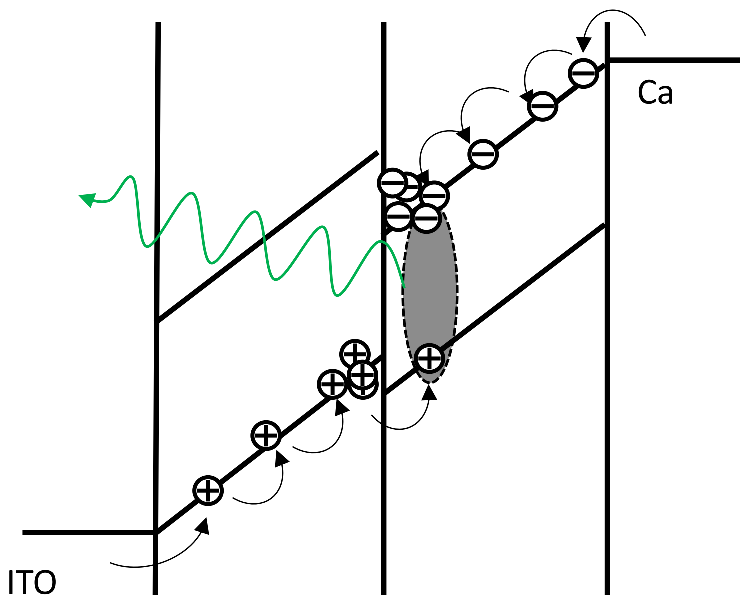




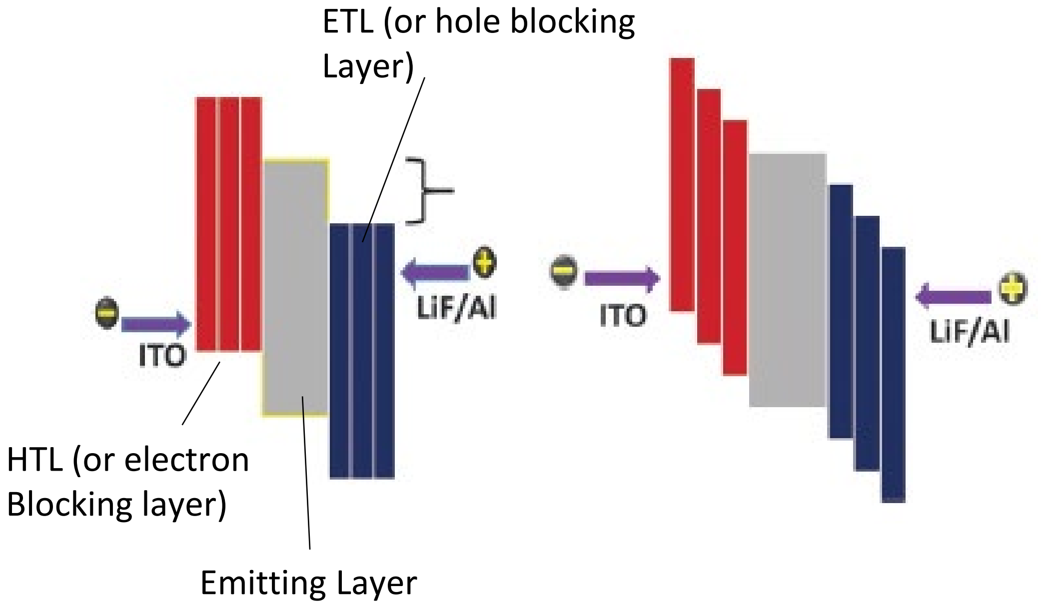
C. W. Tang, S. A. VanSlyke, Appl. Phys. Lett. 51, 913 (1987)

Milestone I: Bilayer (multilayer) device architecture

As we have seen, in principle only one organic layer and two appropriate electrodes are required for electroluminescence. The recombination probability, however, is greatly enhanced when electrons and holes are concentrated in the same volume of the device, since the recombination probability is proportional to the product of the charge densities. A strongly localized recombination zone can be achieved if the hole transporting layer is also an *electron blocking layer* and the electron transport layer is at the same time a *hole blocking layer*. By this way recombination takes place in the middle of the device, which is also the best location from an optical point of view (maximum optical out-coupling) and from a photophysical point of view (excitons will not reach the electrode interfaces, where they are quenched). This device architecture was first introduced by C. W. Tang and S. A. Van Slyke in 1987 (paper cited more than 12000 times as of 2020). A typical bilayer device is shown below.

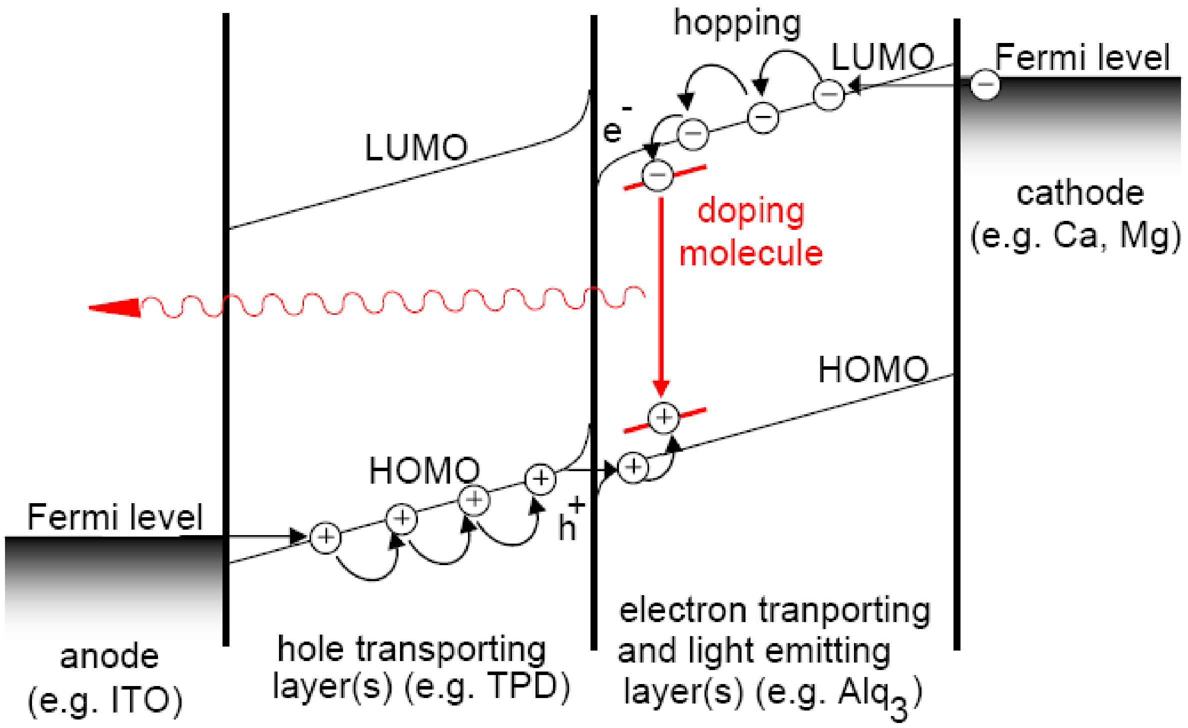


The bilayer device concept can be extended to a three-layer device or multilayer device, where a dedicated emitter layer is sandwiched between one or several hole transporting layers (HTL) or electron transporting layers (ETL). Due to reduced tunneling barriers it is more advantageous to design a cascade – like arrangement (see below).



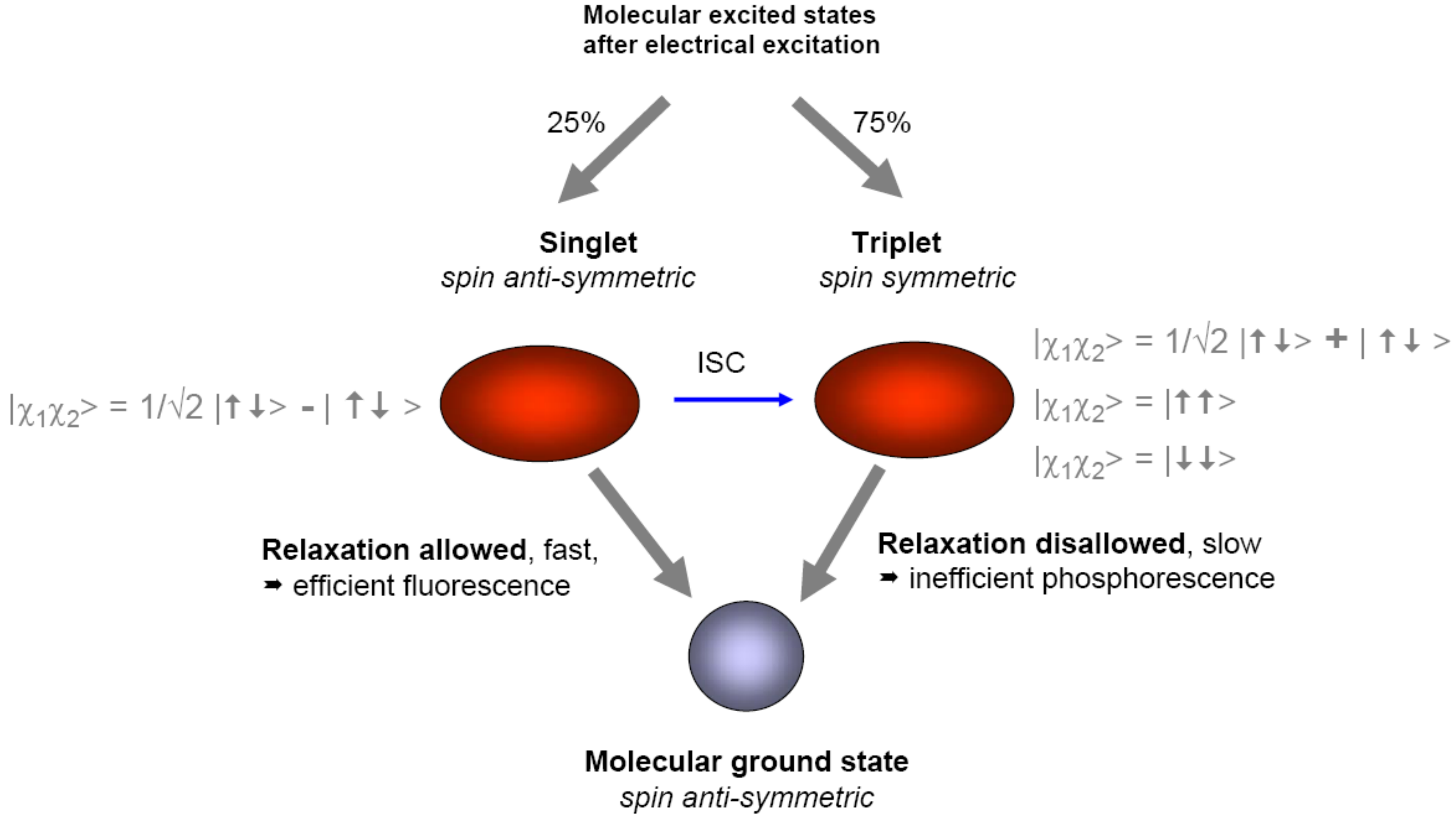
Milestone II: Molecularly doped emitter layer

Only few organic materials have a high luminescence quantum yield in the solid state, even though their fluorescence quantum efficiency in solution is unity. This comes from the fact that molecular aggregation leads to excitonic states with forbidden radiative transitions. There is a trick to get very high emission in these materials nevertheless: A highly luminescent guest molecule is doped into the host layer (about 1%). By energy transfer, all excited states produced in the host layer will be transferred to a nearby guest dopant. This may happen either by energy transfer (Förster type, Dexter type) or direct recombination on the guest. In the figure below, the direct recombination mechanism is schematically drawn. Of course, the emission wavelength will now correspond to the luminescence of the doping molecule and not to the host material. If the doping concentration is too small or in the case of saturation, light-emission from the host is also observed.



Milestone III: The singlet-triplet problem

Upon absorption of a photon, a singlet excited state is created given the fact that the ground state of a conjugated molecule or polymer is also a singlet (spin conservation rule). On the contrary, when excited states are created by the recombination of positive and negative charge carriers, a statistical distribution of singlet and triplet states is obtained. According to the scheme below, 25% of fluorescent singlets and 75% of non-emissive triplet states are obtained. Accordingly 3/4 of all excitons formed by recombination are not contributing to the luminescence of the device. In order to harvest the luminescence of triplet excited states, two major strategies have been followed, **triplet emitters** and **thermally activated delayed fluorescence** (TADF).



Molecular excited states after electrical excitation

25%

75%

Singlet
spin anti-symmetric

Triplet
spin symmetric

$|\chi_1\chi_2\rangle = 1/\sqrt{2}\,|\uparrow\downarrow\rangle - |\uparrow\downarrow\rangle$

ISC

$|\chi_1\chi_2\rangle = 1/\sqrt{2}\,|\uparrow\downarrow\rangle + |\uparrow\downarrow\rangle$

$|\chi_1\chi_2\rangle = |\uparrow\uparrow\rangle$

$|\chi_1\chi_2\rangle = |\downarrow\downarrow\rangle$

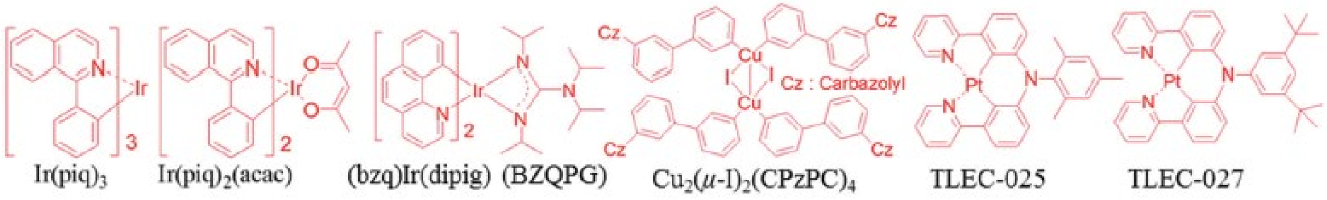
Relaxation allowed, fast,
➡ efficient fluorescence

Relaxation disallowed, slow
➡ inefficient phosphorescence

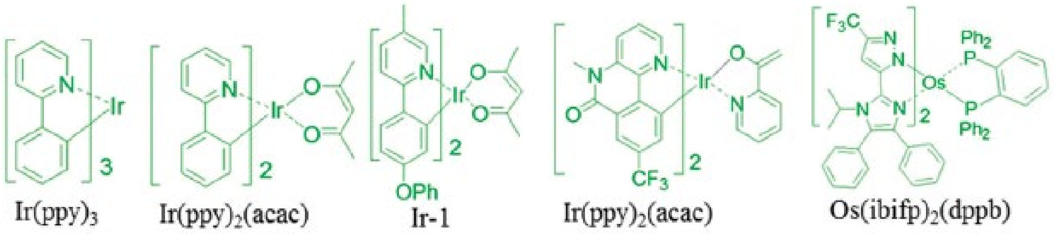
Molecular ground state
spin anti-symmetric

Triplet emitters

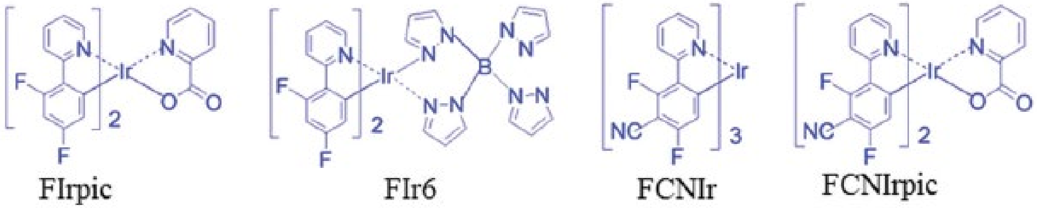
We have learned that an optical transition must conserve spin. Therefore luminescence from a triplet state is forbidden meaning that luminescence lifetimes would be so long that non-radiative relaxation processes would dominate. However, spin-orbit coupling can induce mixing of triplet and singlet states and therefore, if heavy atoms are present in the molecular structure, the excited state is no longer a pure triplet state, but rather a mixture of singlet and triplet states with a much enhanced radiative rate constant. M. A. Baldo in 1998 first came up with a Pt-ligand complex which was used in the same way as a fluorescent dopant. Later on many further metal – ligand complexes were designed (see below) and allowed to boost the luminous efficiency to above 100 cd/W.



red emitters



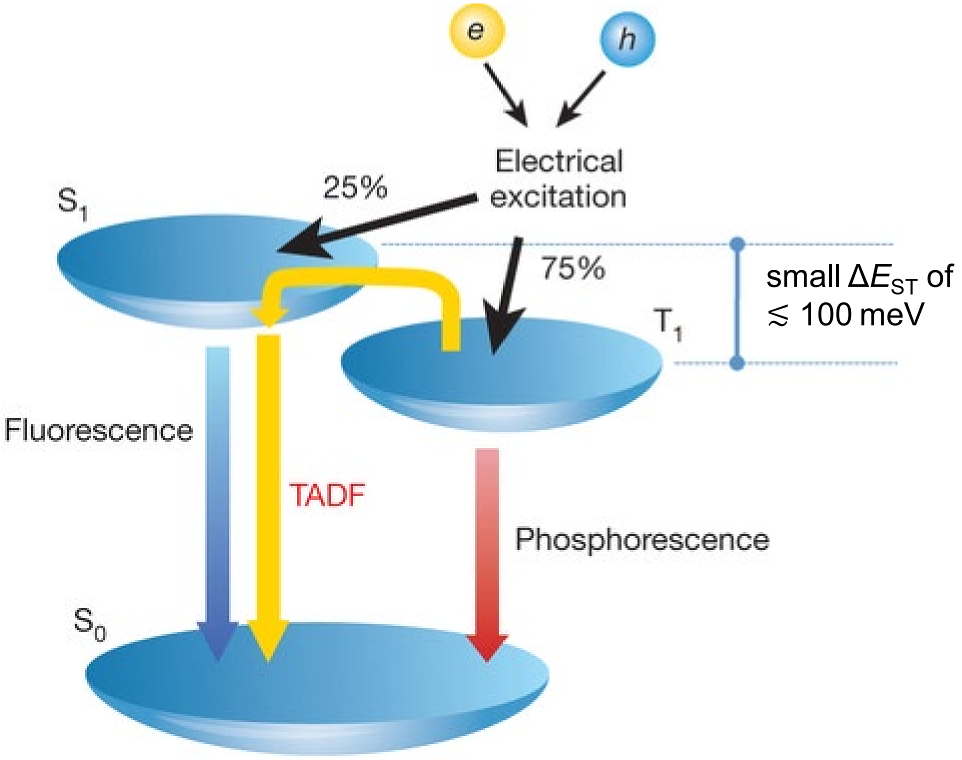
red emitters



blue emitters

J. H. Jou et al., *J. Mater. Chem. C,* 2015, 3, 2974--3002

Thermally activated delayed fluorescence (TADF)



The exchange integral ΔE_{ST}:

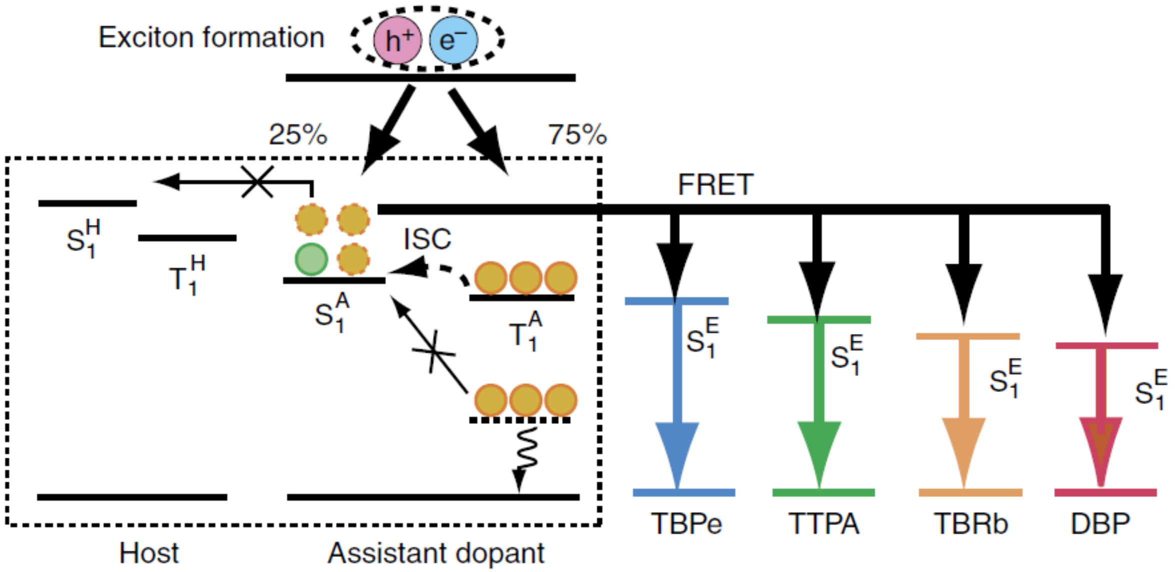
If the electron frontier orbital wavefunctions ψ_{HOMO}, ψ_{LUMO}, can be written as a product of spatial (φ) and spin (S) wavefunctions, e.g. $\psi_{HOMO} = \varphi_{HOMO}(r) \cdot S_{HOMO}(s)$, where s can take the value α or β, ΔE_{ST}:can be written as:

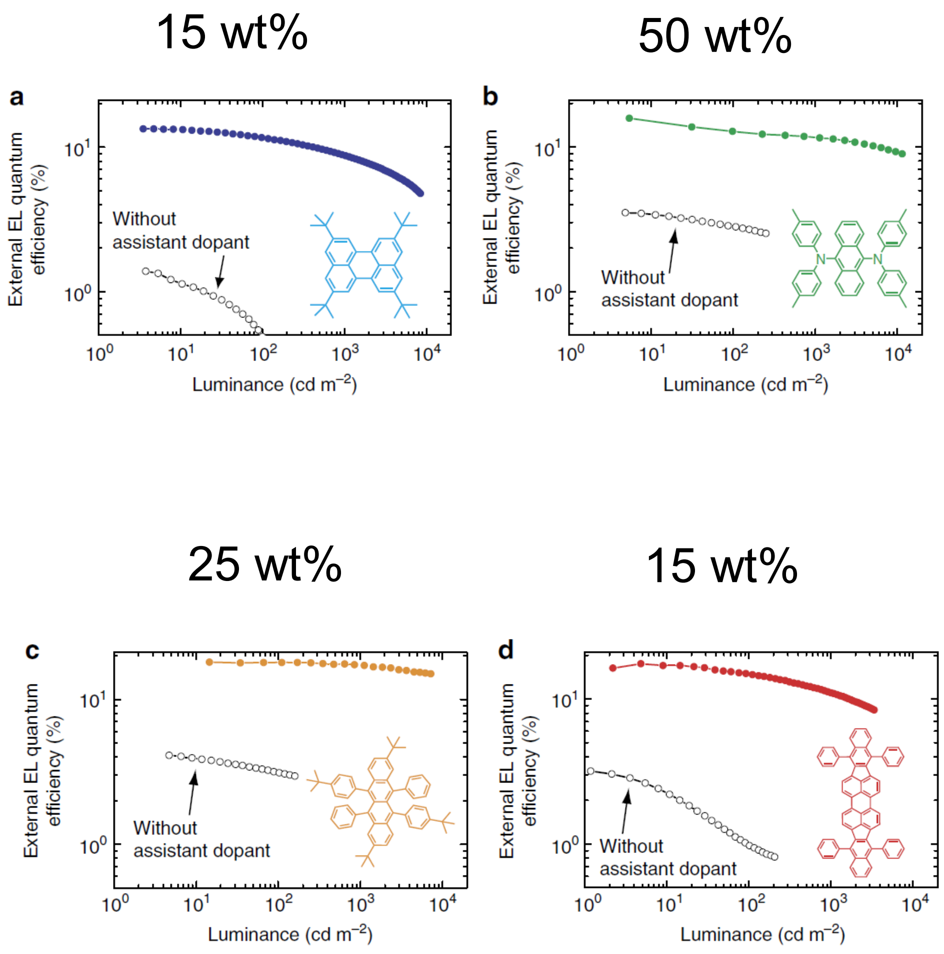
$$\Delta E_{ST} = \int_1 dr_1 \int_2 dr_2 \frac{2e^2}{r_1 r_2} \varphi_{HOMO}(r_1)\varphi_{LUMO}(r_2)\, \varphi_{HOMO}(r_2)\varphi_{LUMO}(r_1)$$

Therefore, ΔE_{ST}:is small when the overlap between φ_{HOMO} and φ_{LUMO} is small. Note that the exchange interaction has its origin in the fact that QM imposes antisymmetric wavefunctions for fermions.

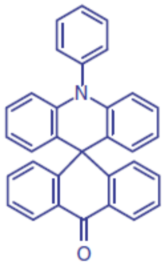
The idea of TADF was introduced by Endo in 2009, but only since in 2012 when C. Adachi reported efficiencies as high as for triplet emitters the strategy became a real alternative. The process is based on reverse intersystem crossing (RISC) from T$_1$ to S$_1$. As illustrated in the scheme above this process greatly depends on the magnitude of the exchange energy DE_{ST} which should be smaller than 100 meV in order to obtain good yields at room temperature. The exchange energy is very much dependent on the overlap of HOMO and LUMO and therefore push pull molecules with an (internal) charge transfer transition are good candidates for this mechanism. Other possibilities are charge transfer excitons between two different molecules (so called exciplexes) which are as well interesting candidates for TADF.

TADF using assistant dopant fluorescent molecules (hyperfluorescence)

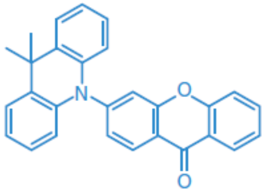




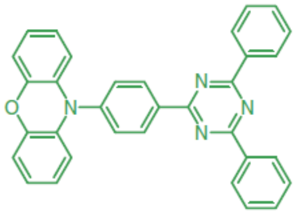
Assistant dopant



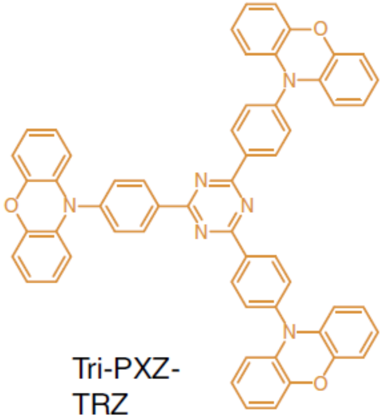
ACRSA



ACRXTN



PXZ-TRZ

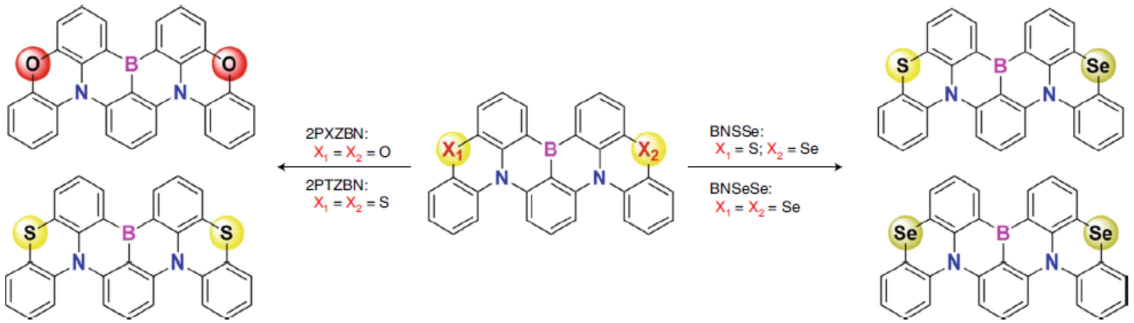


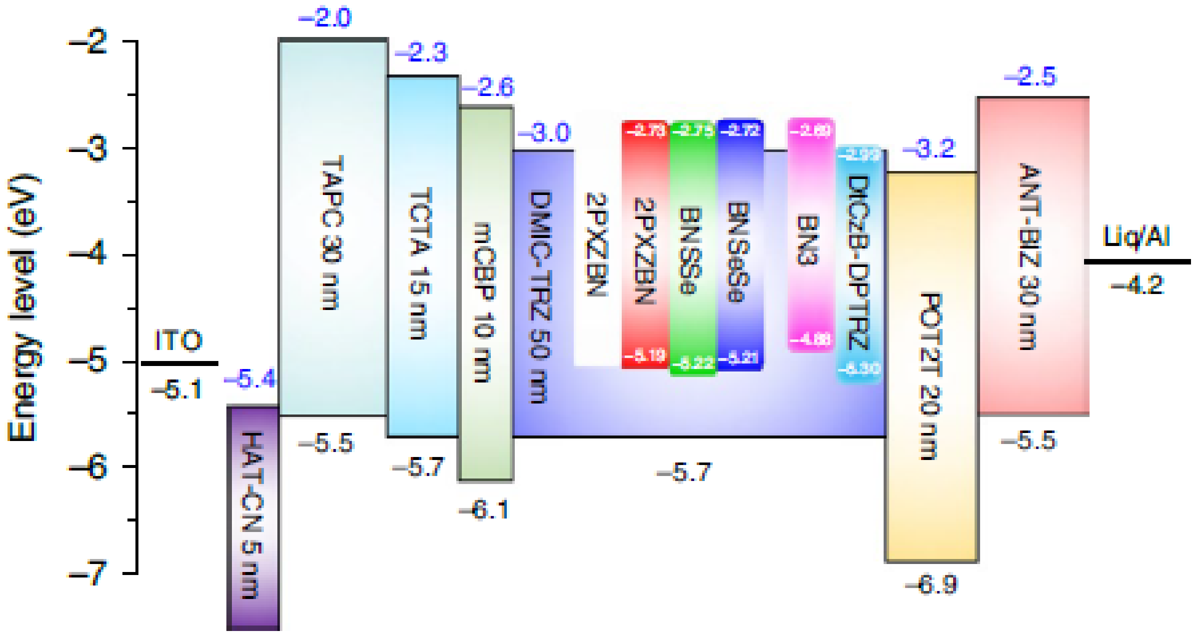
Tri-PXZ-TRZ

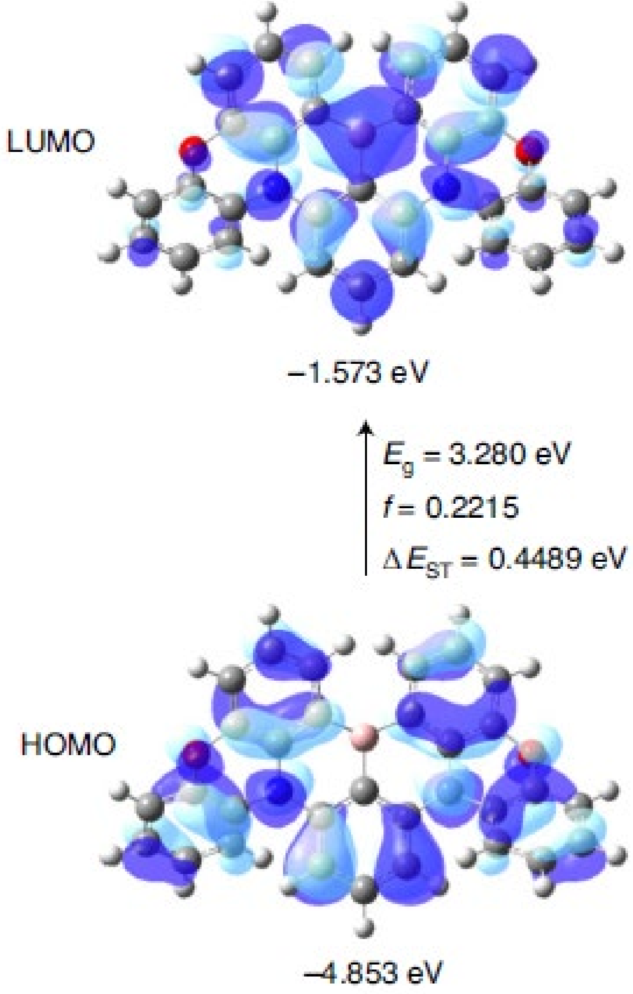
C. Adachi, Nature Comm. 2014

Exciton generation efficiency reached nearly 100% …

Multi-resonance thermally activated delayed fluorescence emitters with an efficient reverse intersystem crossing process







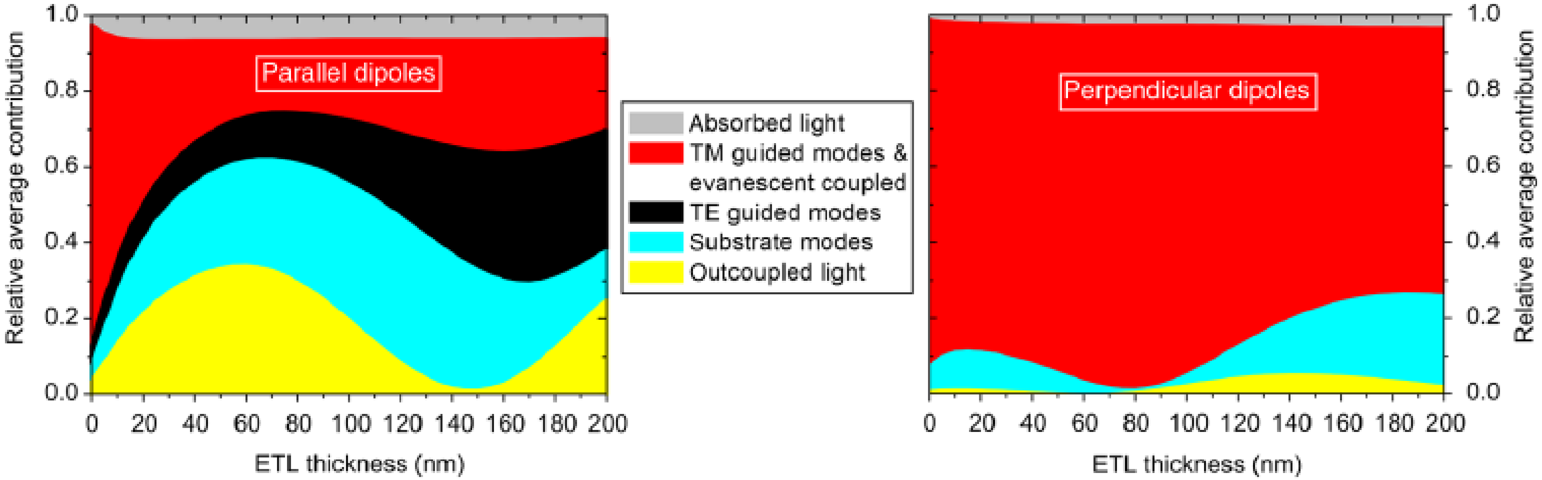
Using a fluorescent emitter (HF **BN3**) a super high performance could be achieved at maximum:

current efficiency of **164.5 cd/A**, luminous efficacy: **205.8 lm/W**, EQE **40.5 %**

Y. X. Hu. et al., *Nature Photonics,* 2022, 803–810

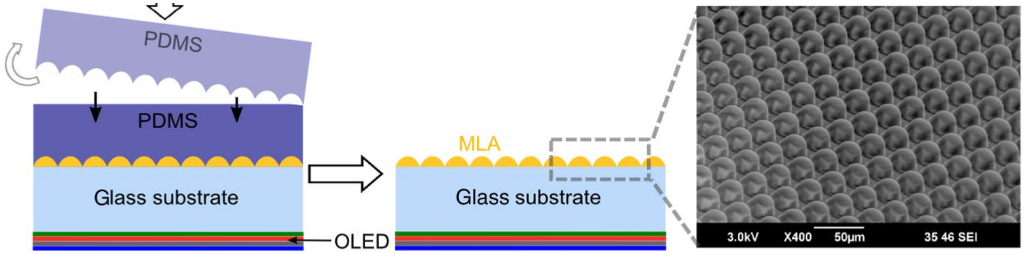
Milestone IV: optical engineering

The out-coupling of light out of the thin film device does not receive the full attention it deserves. As a matter of fact, only about 20% of all photons emitted from the emitter layer of a typical OLED are able to escape into half space. All other photons are guided to the edges where they are not useful for the luminescent device. As can be inferred from the figure below, tuning the thickness of the stacked layers in the device, can already produce significant out-coupling improvements.

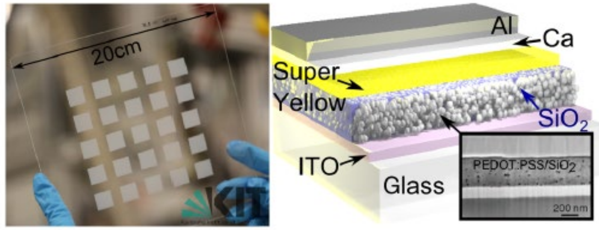


There are further strategies to optimize out-coupling. They are based on microlens arrays or scattering layers.

microlens arrays



scattering layers



G. Gomard et al., J. Photon. Energy 6(3), 030901 (2016)