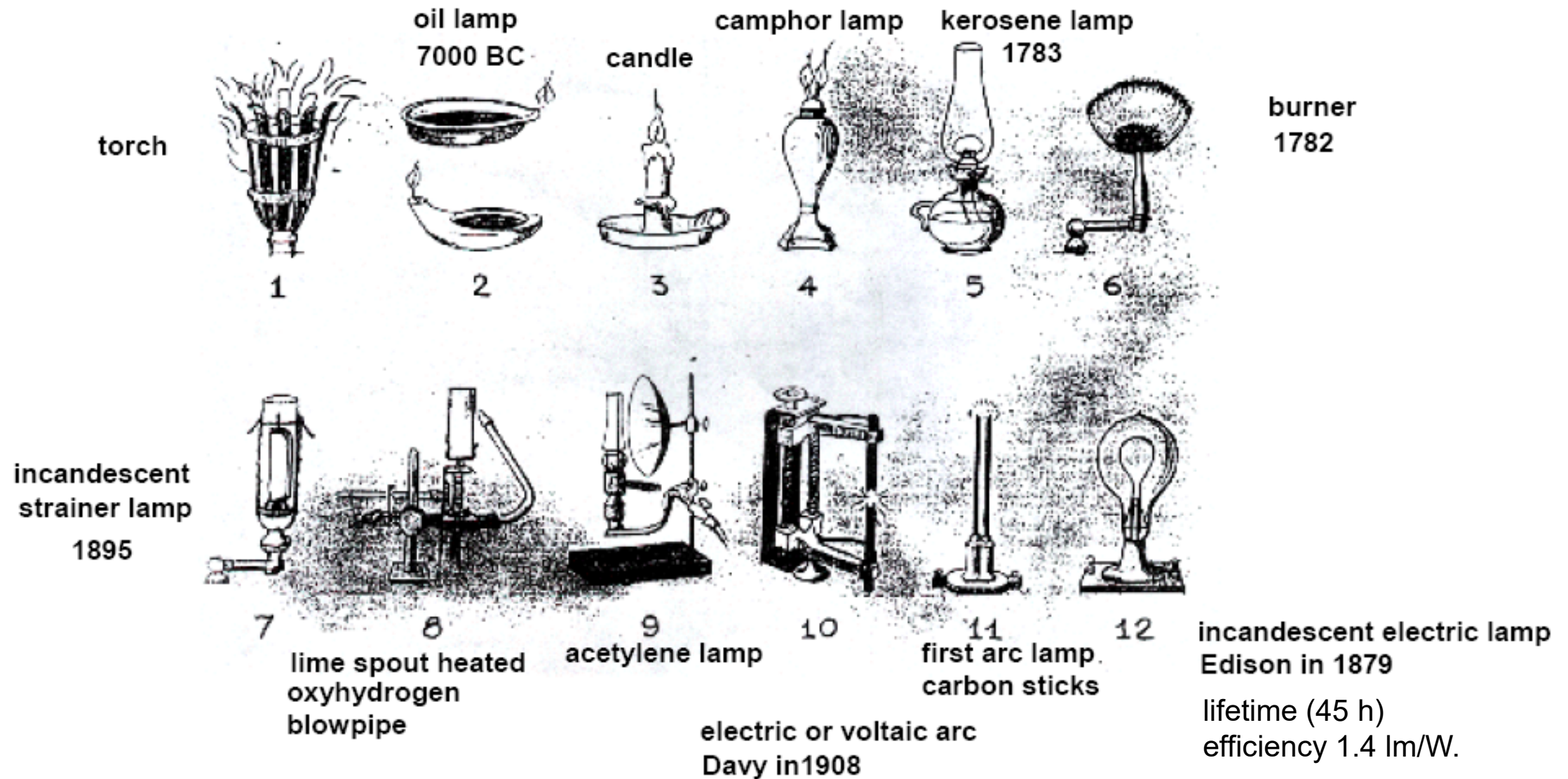


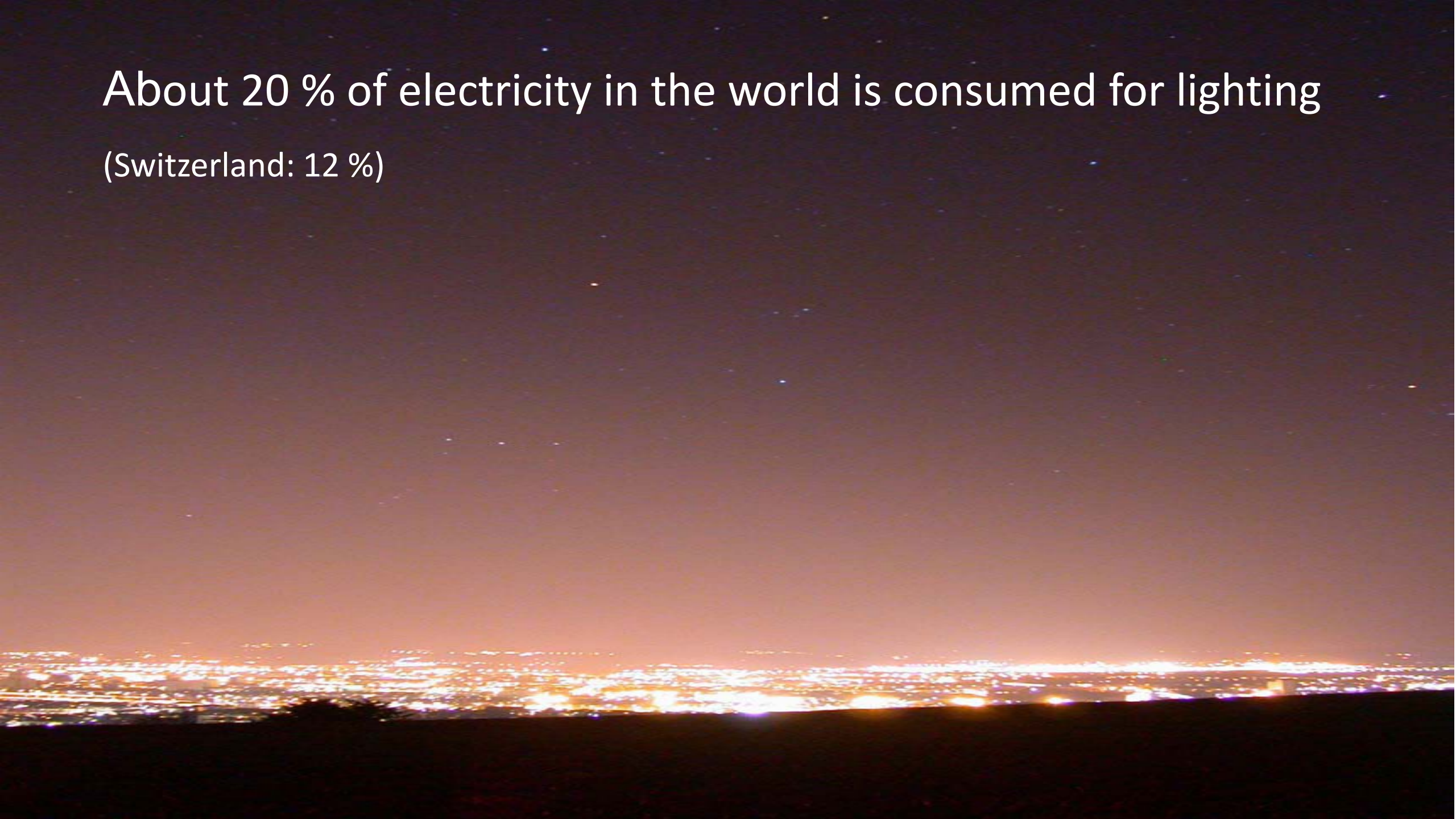
7.5 Organic light-emitting devices (OLEDs)

A short history of lighting devices



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

(Switzerland: 12 %)



Commercial sources



Halogen

72 W
5000 h
20 lm/W



LED

14 W
30 000 h
100 lm/W



incandescent
(fading out)

100 W
1000 h
15 lm/W



CFL

23W
10000 h
60 lm/W to 80 lm/W (tube)

OLED Displays

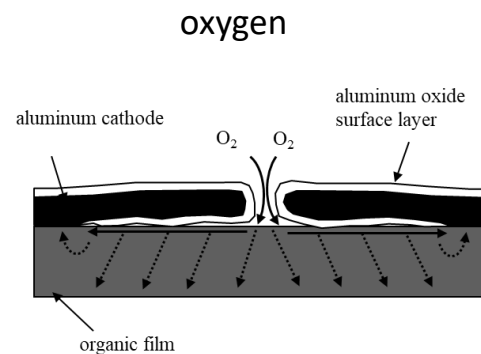
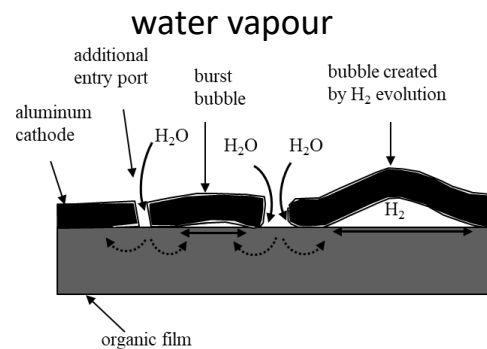
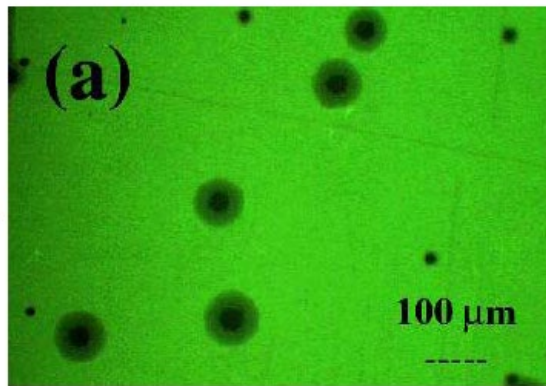
(15% of the display market share, 65% of the smartphone display market share in 2021)



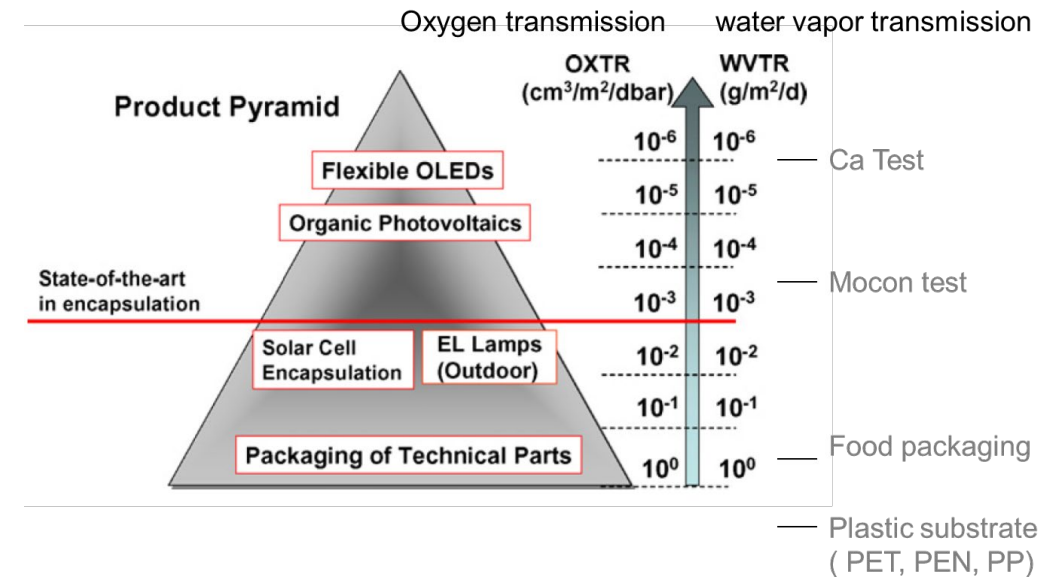
The importance of encapsulation

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

dark spot formation

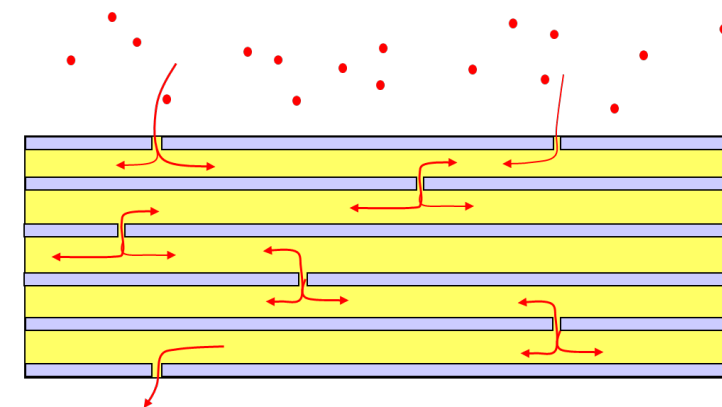


M. Schaer, F. Nüesch, D. Berner, W. Leo, L. Zuppiroli, *Adv. Func. Mater.*, 11 (2), (2001), p.116-121.



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

Basic strategy for flexible barrier foils:



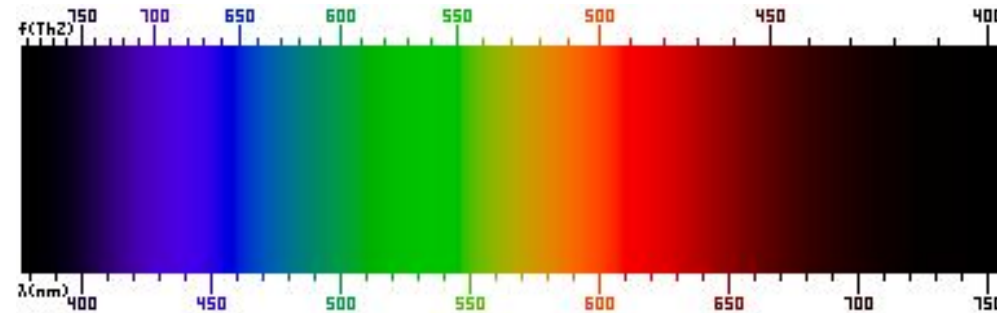
- Metal or metal oxide
- Polymer layer

➡ Long diffusion paths

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 :

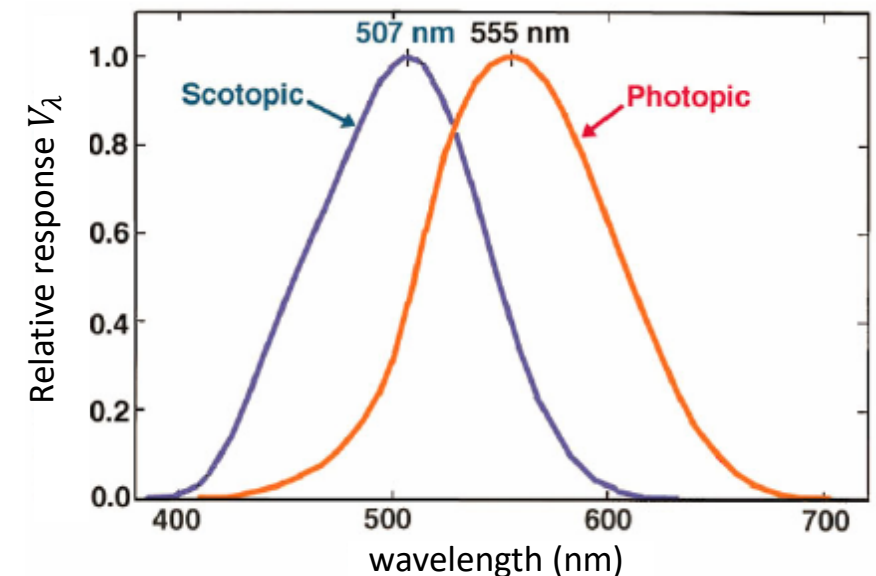
$$\nu = \frac{c}{\lambda}$$



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/m². Candela (cd) are lumen/steradian (lm/sr) and are related by the following formula:

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

Photometric power emitted by a source

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

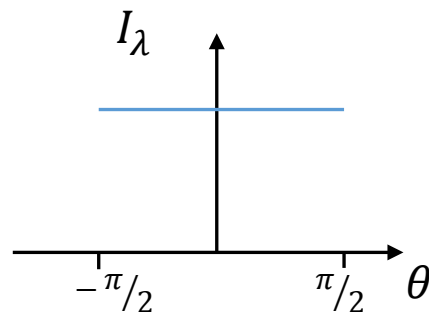
$$\Omega = \frac{A}{r^2} = 2\pi(1 - \cos\theta)$$

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

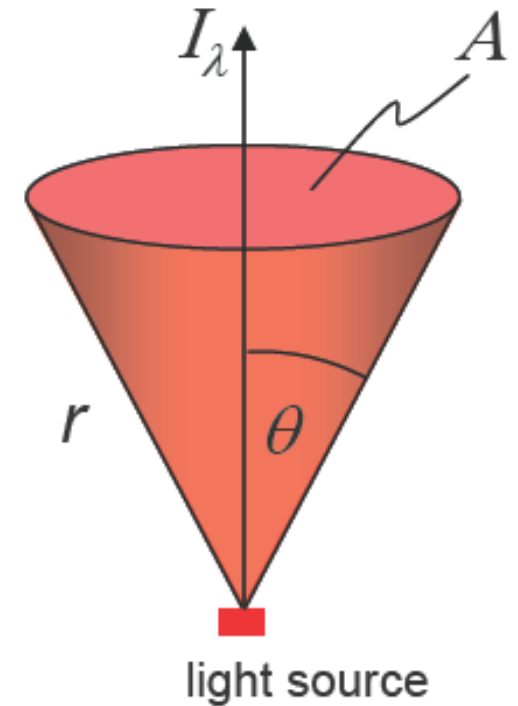
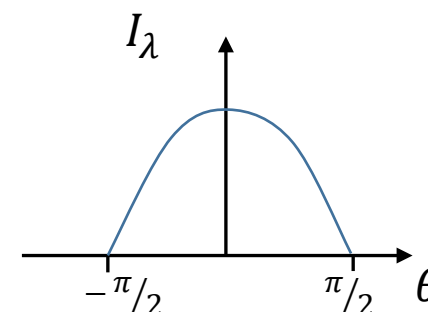
Isotropic emitter (half space)

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



Lambertian emitter (half space)

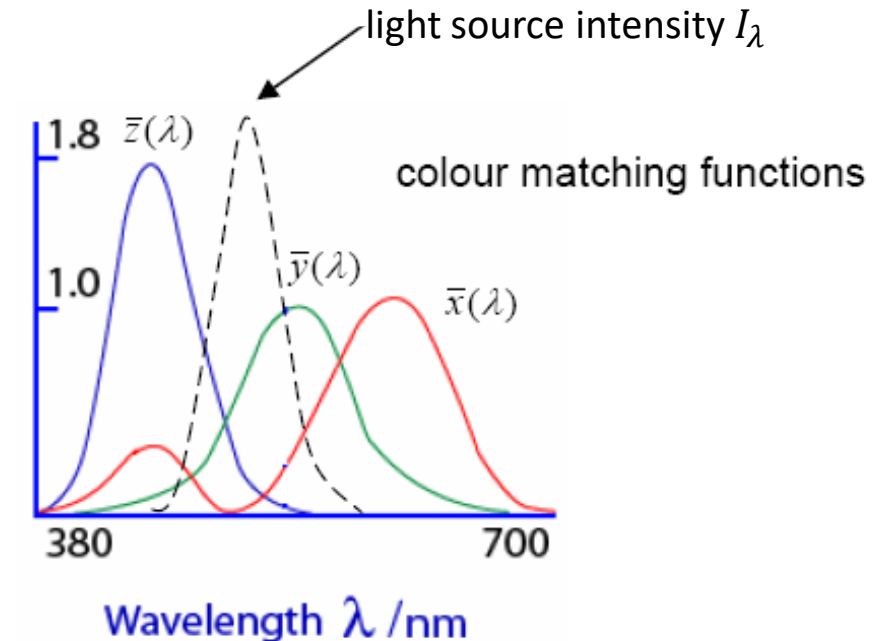
$$\phi_{\lambda}[lm] = I_{\lambda}^{cand}(0) \pi$$



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 Internationale de 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:

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

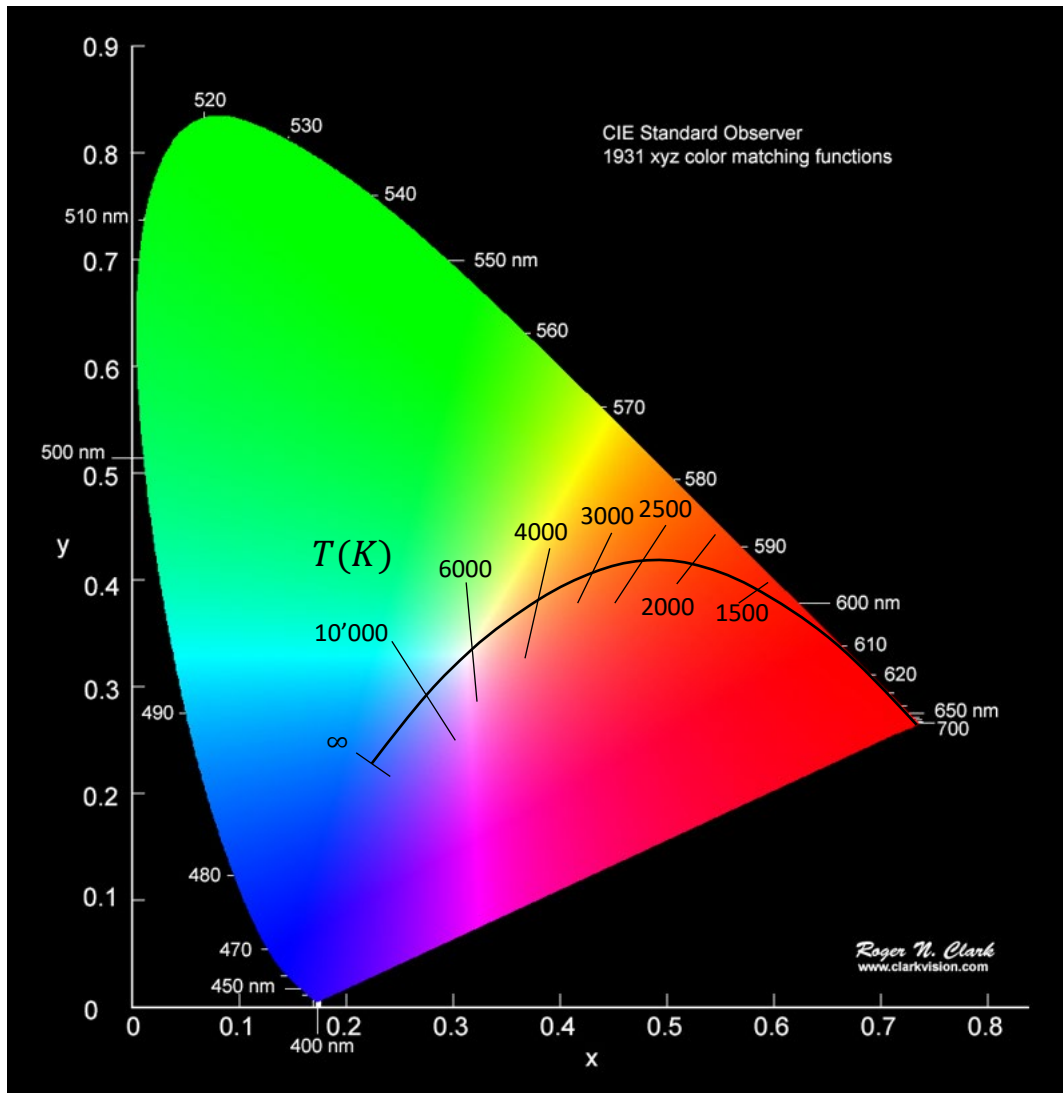


Based on these functions, the chromaticity coordinates which reflect the perceived colour are defined as normalized values:

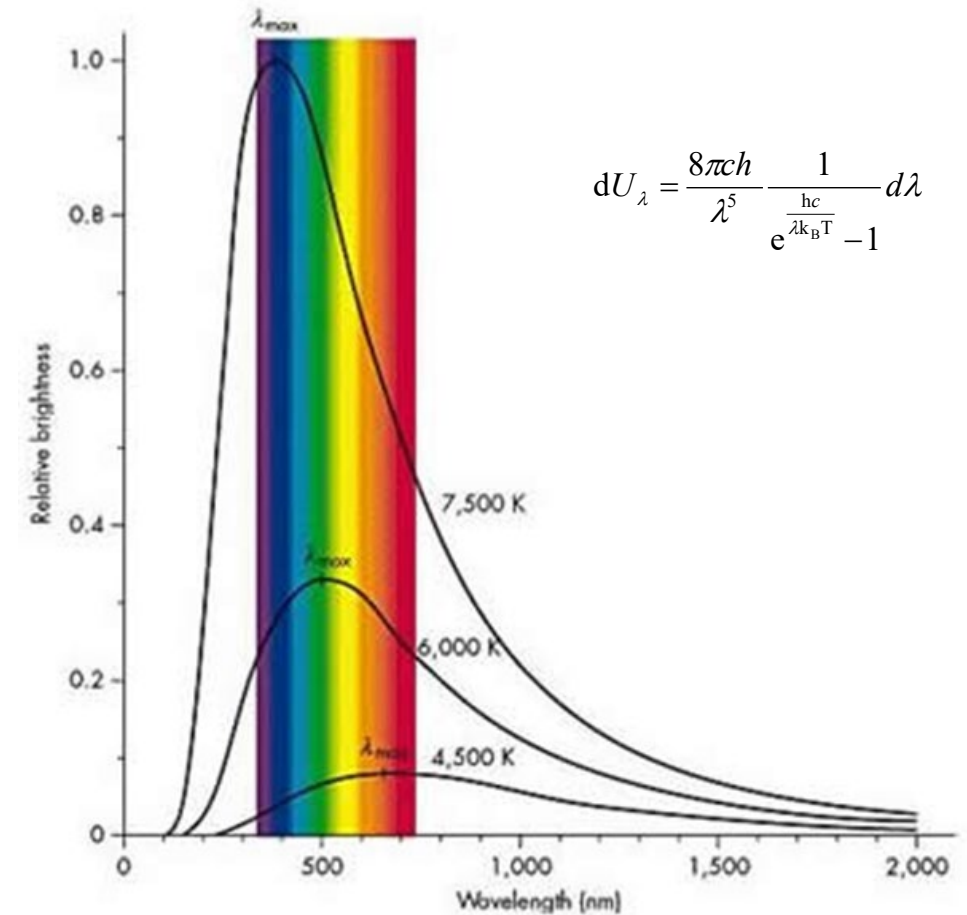
$$x = \frac{X}{X+Y+Z} \quad y = \frac{Y}{X+Y+Z} \quad z = \frac{Z}{X+Y+Z}$$

Therefore only two coordinates 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.

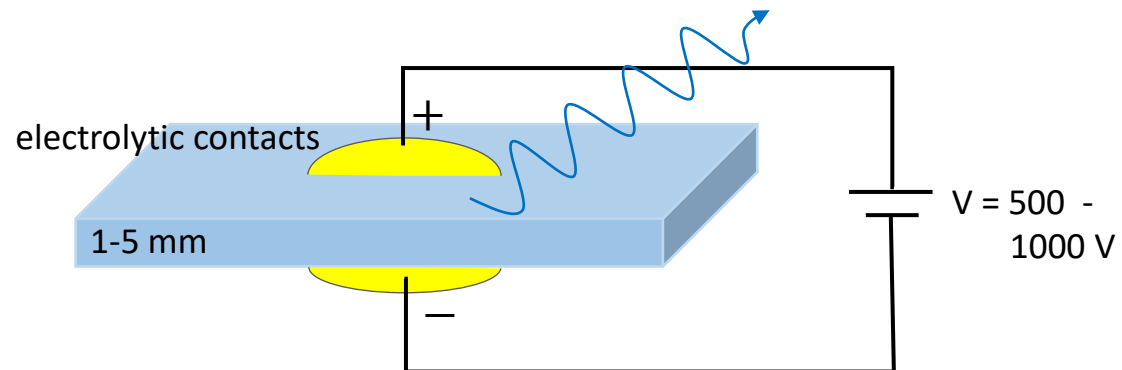
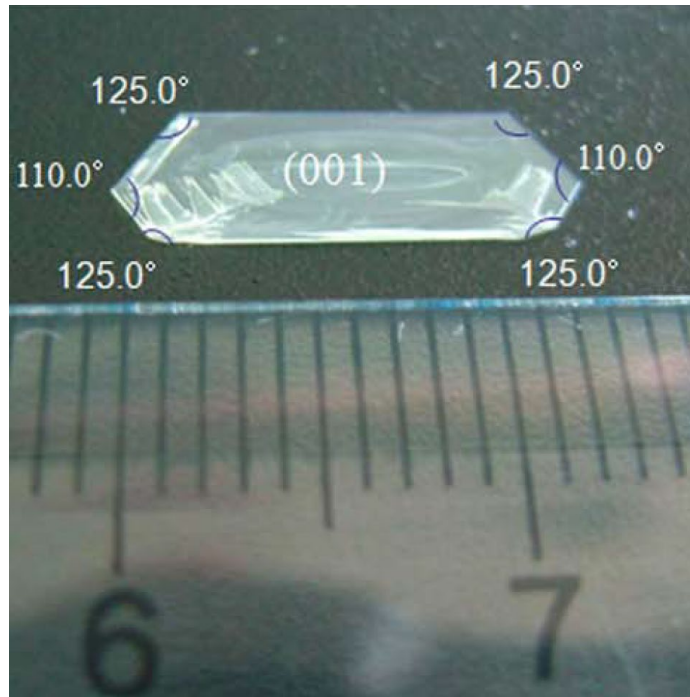


Color temperature

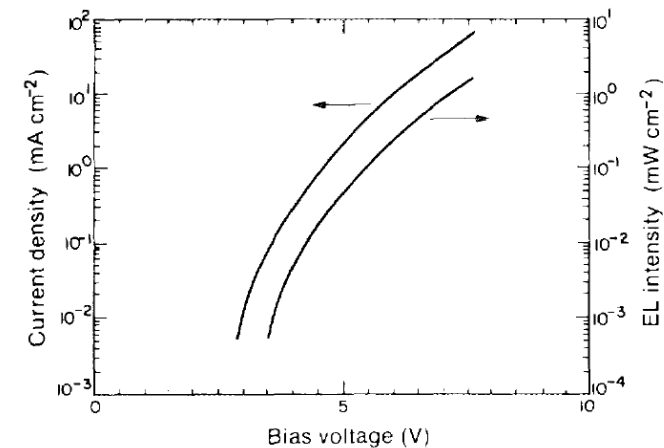
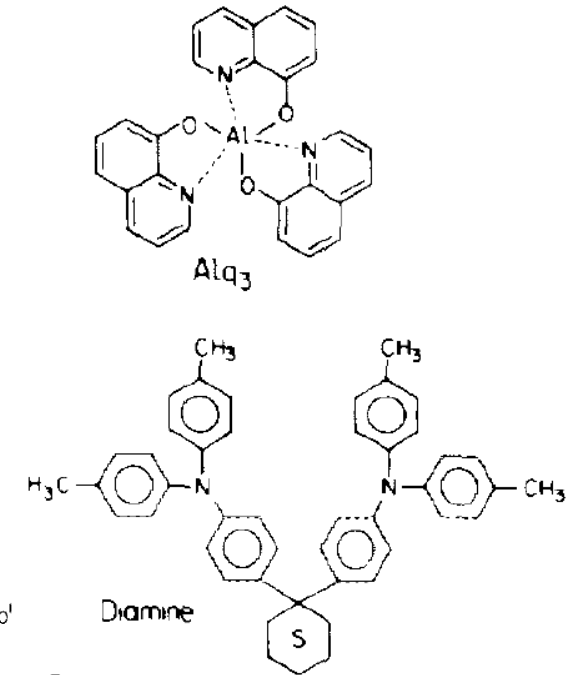
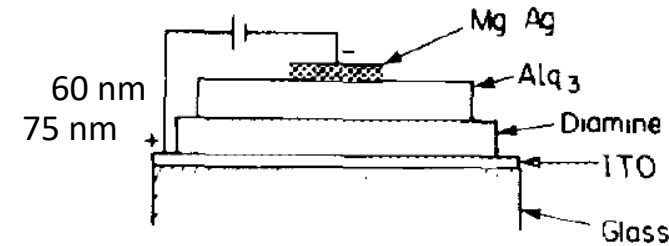


It is interesting to note that the chromaticity diagram not only permits to analyze colour of an emitter, but also permits to synthesize new colours. For example by using a mixture of two colours it is possible to generate new colours along the line connecting their respective coordinates.

OLED device milestones



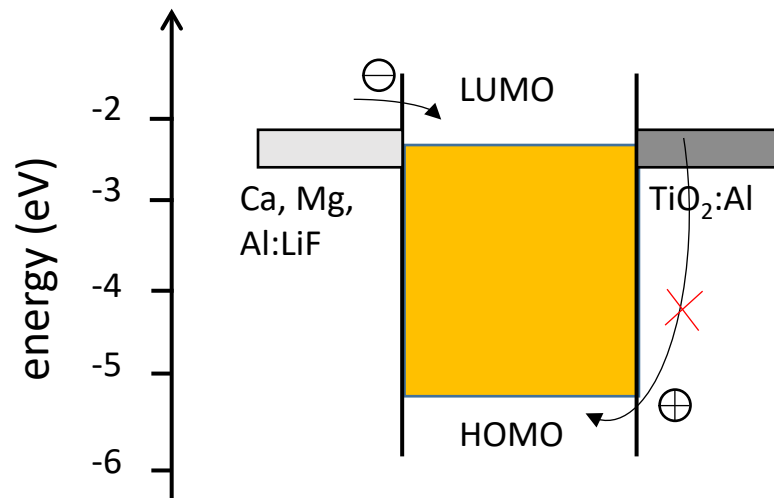
W. Helfrich, W. G. Schneider, Phys. Rev. Lett., 14, 229 (1965)



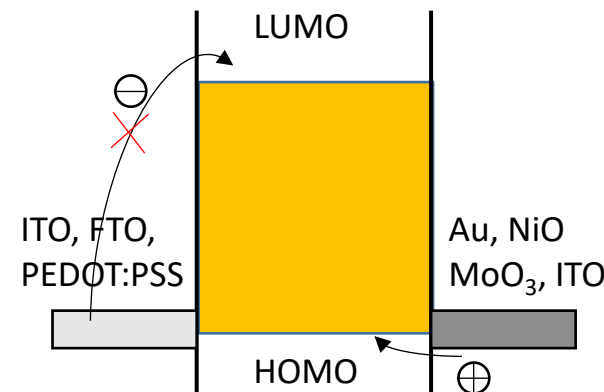
C. W. Tang, S. A. VanSlyke, Appl. Phys. Lett. 51, 913 (1987)

Contacting organic optoelectronic devices

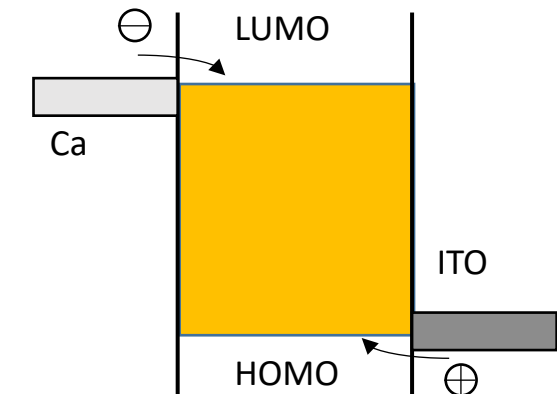
As for inorganic semiconducting devices, contacts to the semiconductor are crucial to device performance. In general, contacts are chosen to provide barrier-free injection of charge carriers into the device. For contacts between metals or between highly doped semiconductors, the Fermi levels align in such away that an efficient electron transfer can occur at the interface. When contacting a semiconductor, highly doped interface layers are usually employed. For organic semiconductors, doping is rarely used. Therefore, the Fermi energy of the contact has to be aligned to relevant molecular orbital, i.e. to the LUMO if electrons are injected or to the HOMO, if holes are injected. Due to the large bandgap of organic semiconductors, specific contacts allow the injection of one type of charge carriers (e.g. electrons into the LUMO) and block injection of the other charge carrier type (e.g. holes into the HOMO). For bipolar injection asymmetric electrodes have to be used. This is illustrated below.



Homopolar «electron-only» device



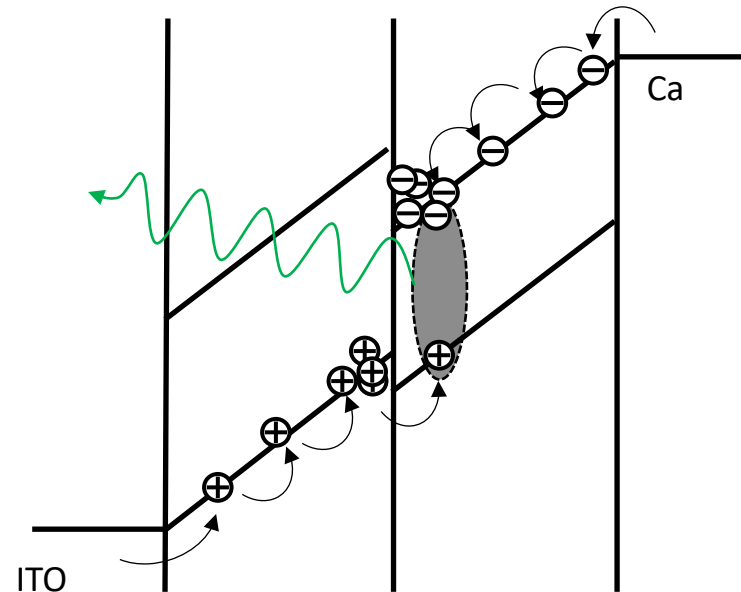
Homopolar «hole-only» device



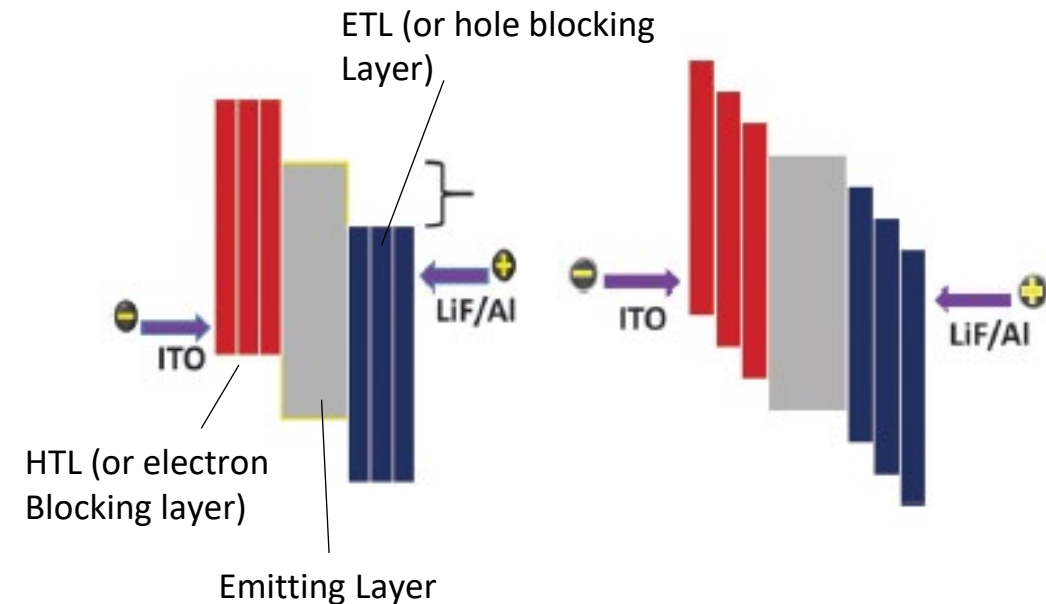
Bipolar device (e.g. for OLEDs)

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.

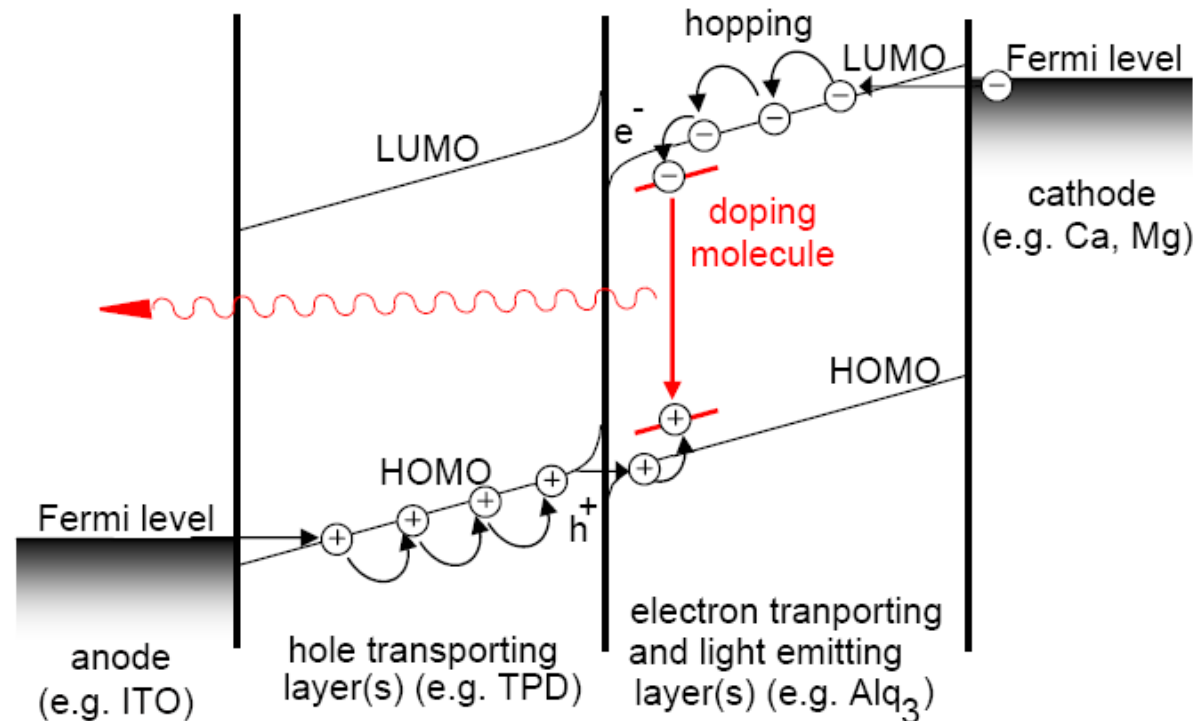


The bilayer device concept can be extended to a three-layer device or multilayer device, where a dedicated emitter layer is sandwiched between one or several hole transporting layers (HTL) or electron transporting layers (ETL). Due to reduced tunneling barriers it is more advantageous to design a cascade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



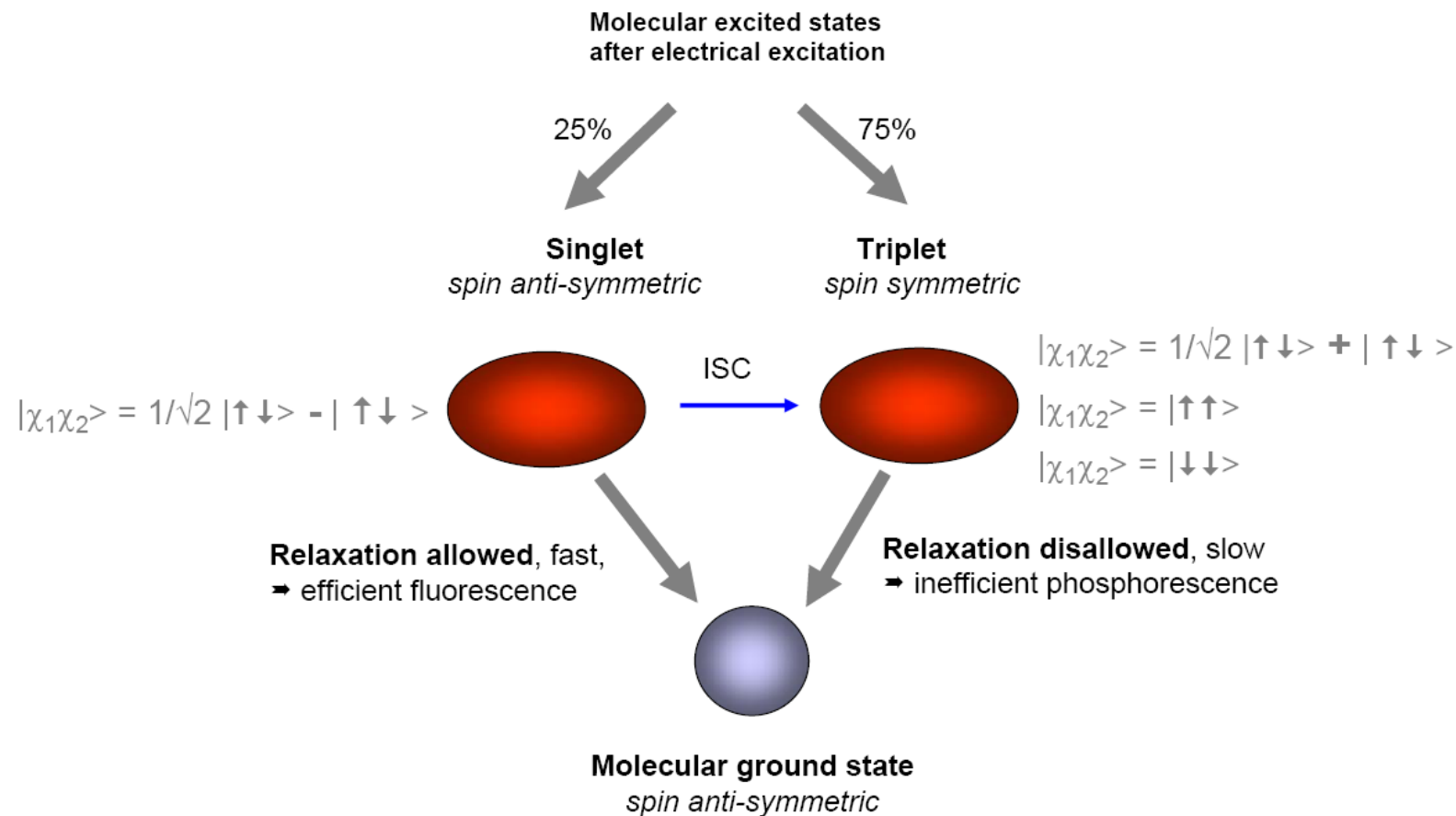
Milestone II: Molecularly doped emitter layer

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.



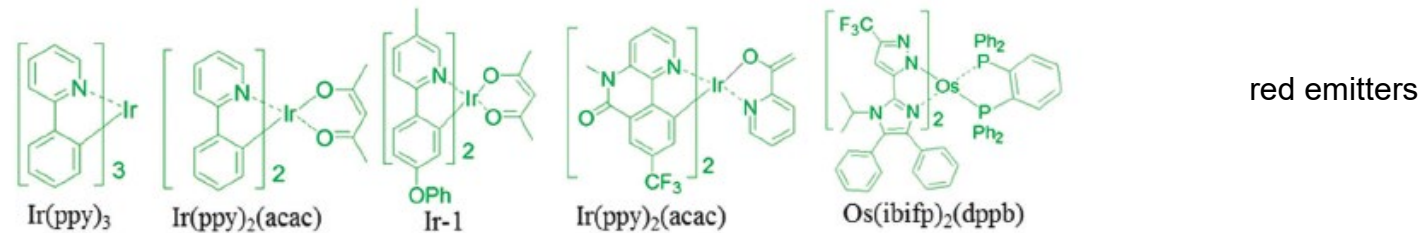
Milestone III: The singlet-triplet problem

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)**.

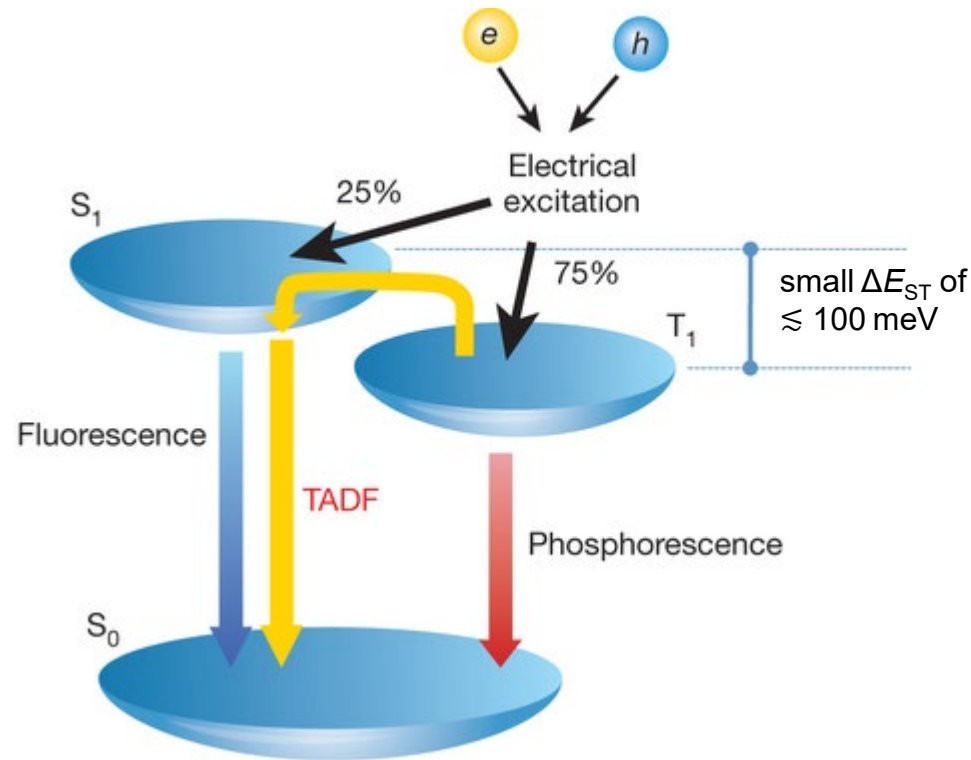


Triplet emitters

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.



Thermally activated delayed fluorescence (TADF)



The exchange integral ΔE_{ST} :

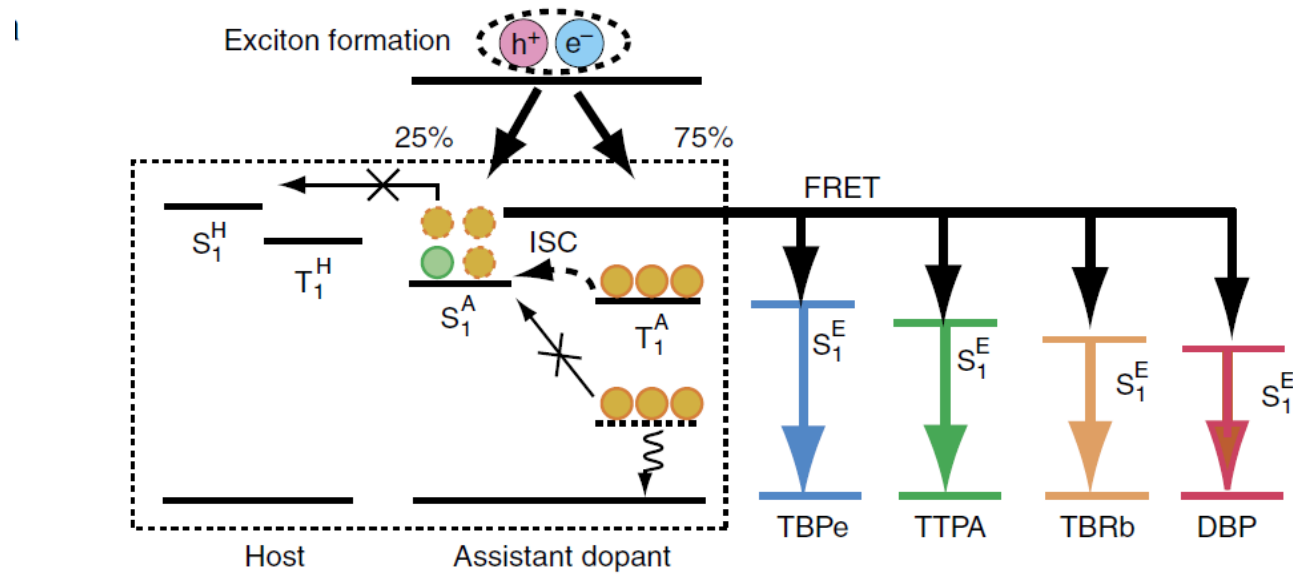
If the electron frontier orbital wavefunctions ψ_{HOMO} , ψ_{LUMO} , can be written as a product of spatial (φ) and spin (S) wavefunctions, e.g. $\psi_{HOMO} = \varphi_{HOMO}(r) \cdot S_{HOMO}(s)$, where s can take the value α or β , ΔE_{ST} can be written as:

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

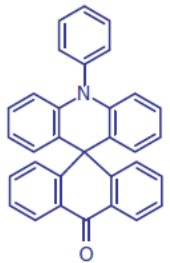
Therefore, ΔE_{ST} is small when the overlap between φ_{HOMO} and φ_{LUMO} is small. Note that the exchange interaction has its origin in the fact that QM imposes antisymmetric wavefunctions for fermions.

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 ΔE_{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.

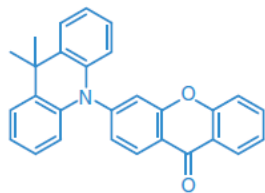
TADF using assistant dopant fluorescent molecules



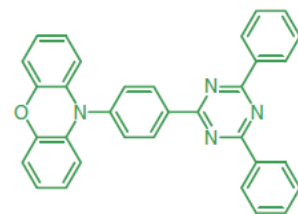
Assistant dopant



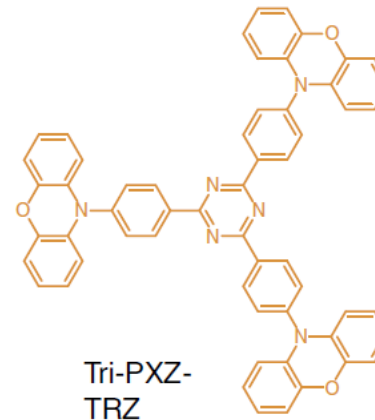
ACRSA



ACRXTN

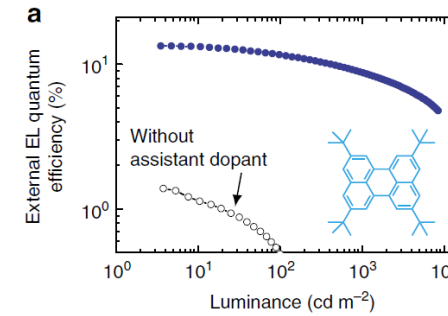


PXZ-TRZ

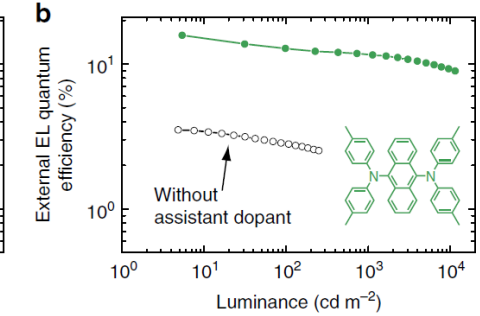


Tri-PXZ-TRZ

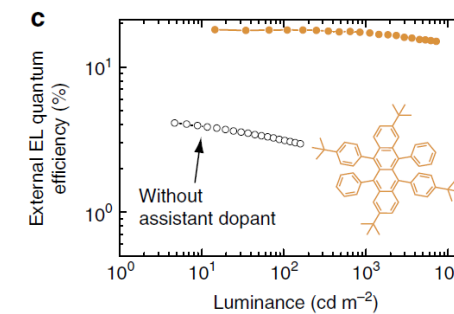
15 wt%



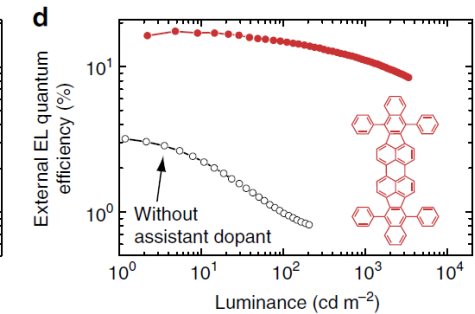
50 wt%



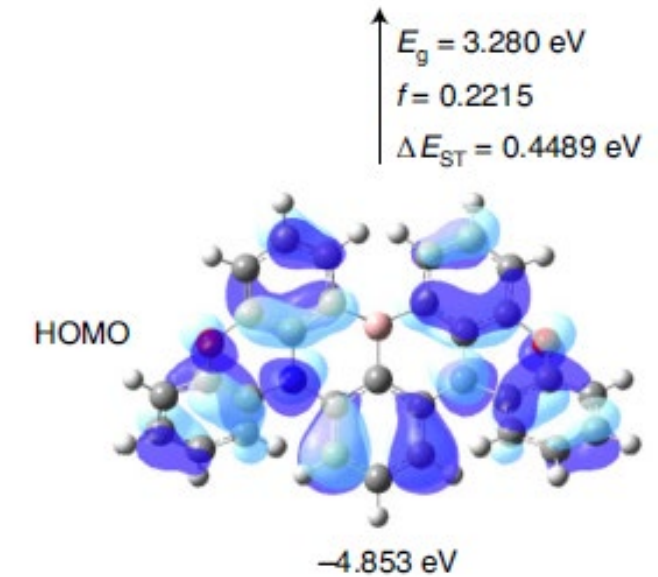
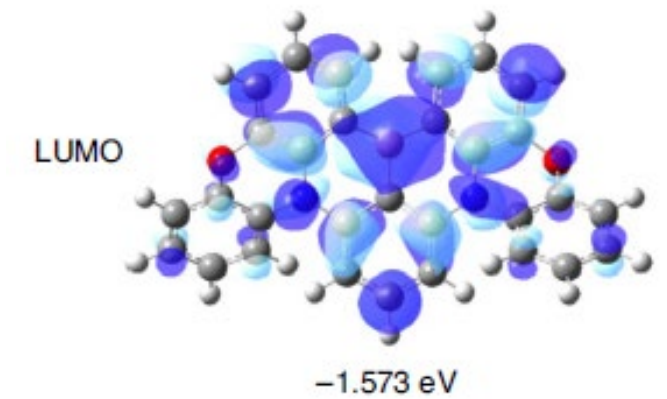
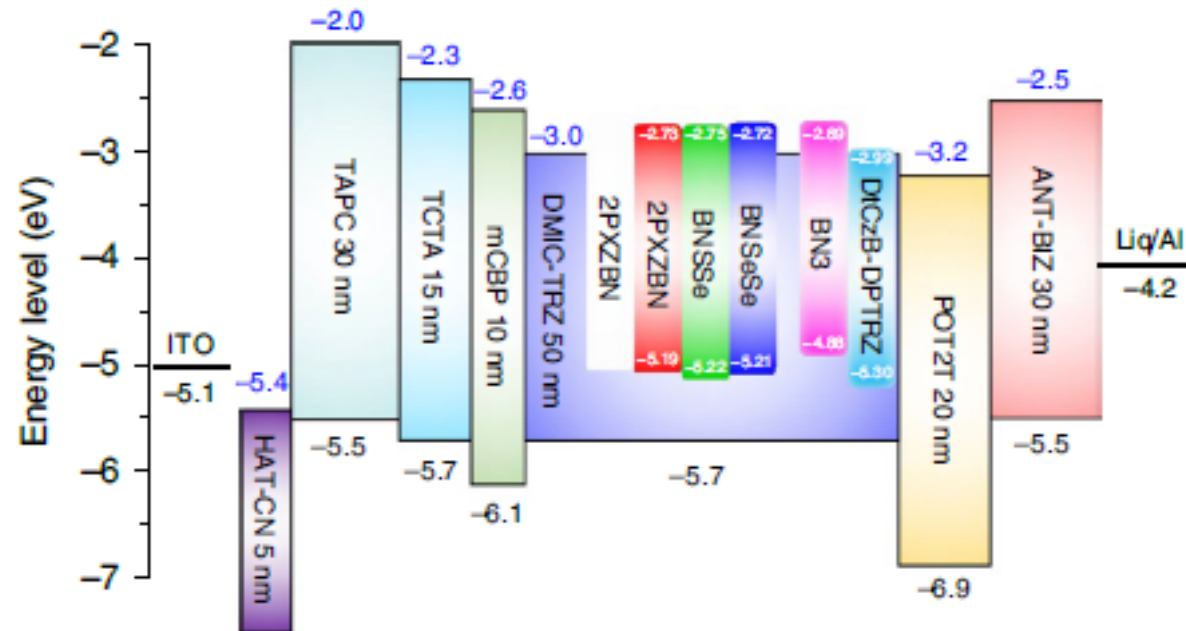
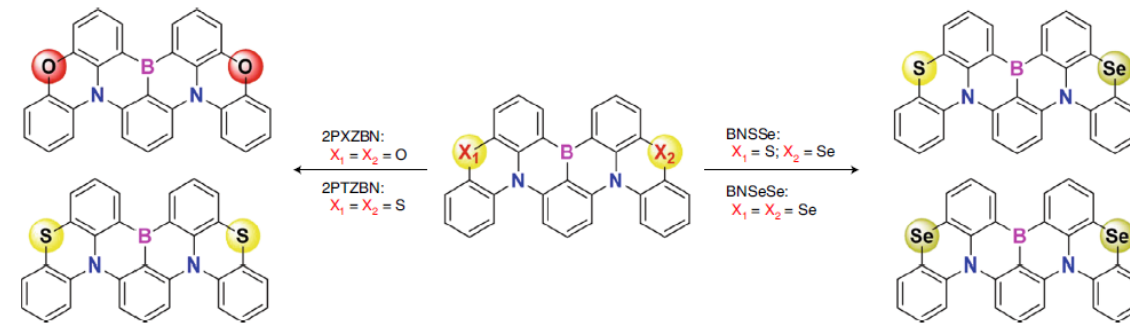
25 wt%



15 wt%



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

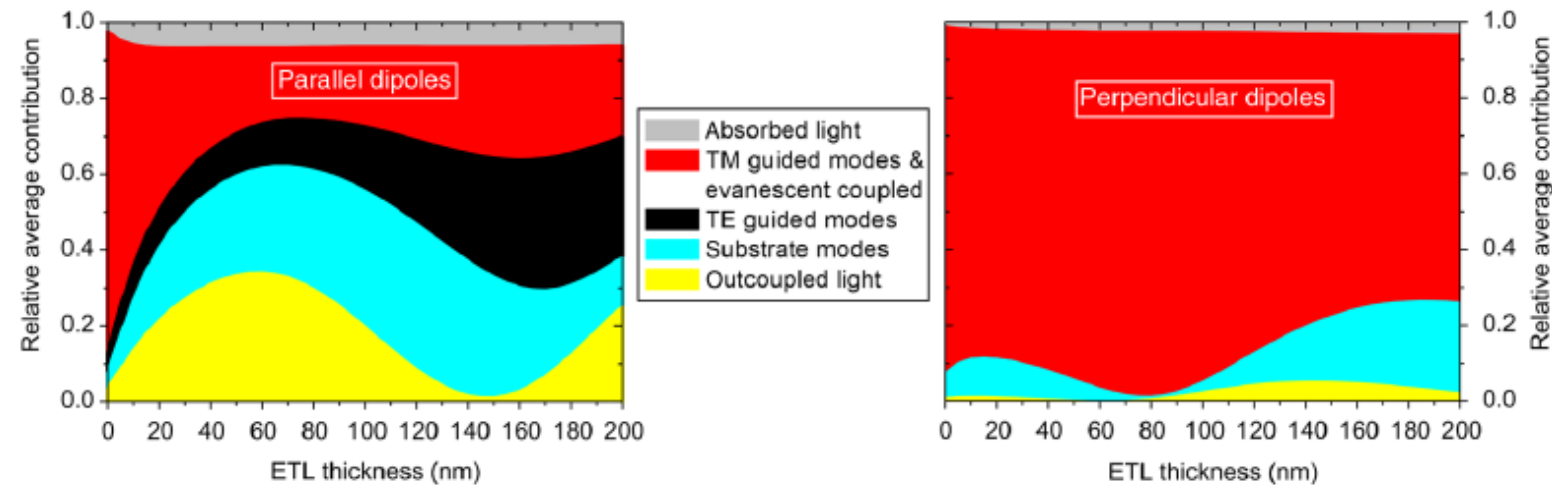


Using a fluorescent emitter (HF **BN3**) a super high performance could be achieved at maximum:
current efficiency of **164.5 cd/A**, luminous efficacy: **205.8 lm/W**, EQE **40.5 %**

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

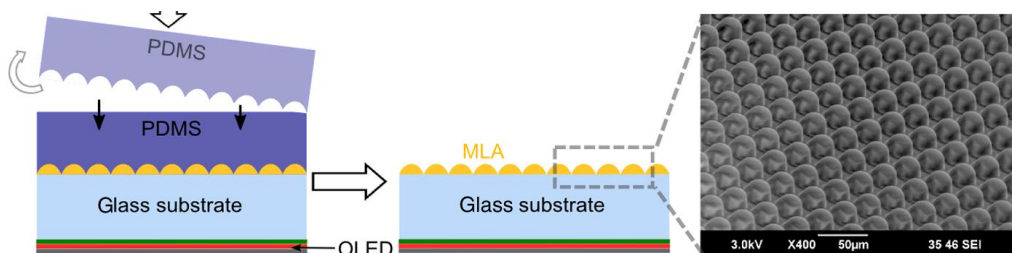
Milestone IV: optical engineering

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.

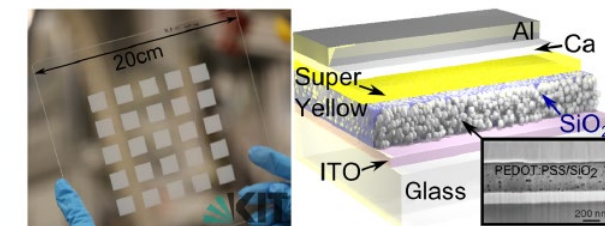


There are further strategies to optimize out-coupling. They are based on microlens arrays or scattering layers.

microlens arrays

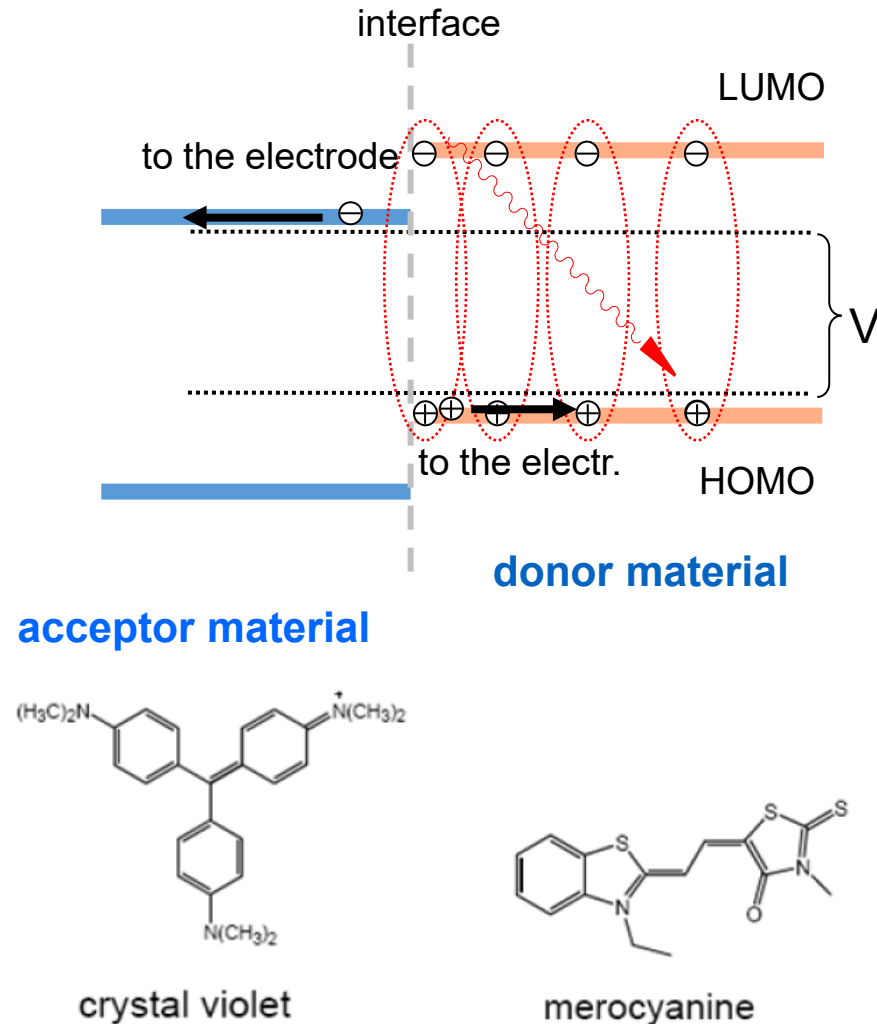


scattering layers



7.5 Organic photovoltaic devices (OPVs)

First report on organic donor-acceptor solar cells



HANS MEIER und A. HAUS, Bamberg: Zum Problem organischer Photodioden (vorgetr. von H. Meier).

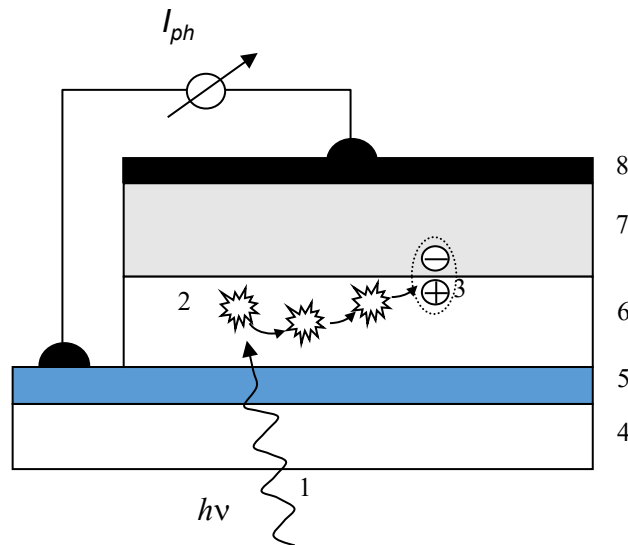
Die Einteilung der photoelektrisch aktiven organischen Farbstoffe in p- und n-Leiter, deren Stromübertragung (wie Messungen der Gasabhängigkeit von Photo- und Dunkelstrom, Thermokraft, Kristallphotoeffekt u. a. beweisen) in der Hauptsache durch Defektelektronen oder Elektronen erfolgt, führte zur Prüfung des organischen pn-Übergangs. In Übereinstimmung zur anorganischen pn-Struktur besitzt ein aus einem p- und n-leitenden Farbstoff zusammengesetztes System (z. B. Merocyanine/Triphenylmethan-Farbstoffe) die Eigenschaft einer Photodiode, die bei Belichtung mit sichtbarer Strahlung einen Kurzschlußstrom I_0 und eine Leerlaufspannung E_{op} ohne äußere Hilfsspannung ergibt. Charakteristische Merkmale dieser Photoelemente sind: Reversibilität von I_0

Hans Meier, Bamberg
1960, Zeitschrift für Elektrochemie

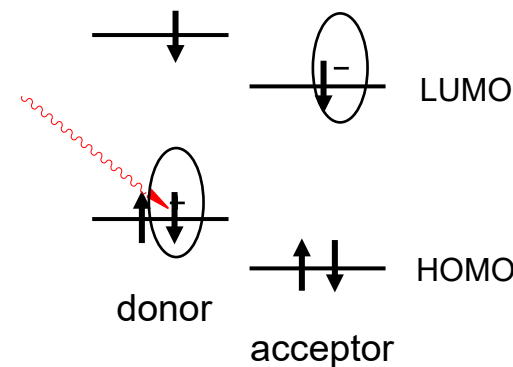
Working principle of organic solar cells

Working principle of a bilayer organic solar cell composed of a transparent substrate (4), a transparent conductive anode (5), an electron donor (6), an electron acceptor (7), and a cathode (8). Upon light absorption (1), excitons (2) diffuse until they recombine or reach the organic heterointerface where charge generation into free electron and holes takes place (3). Due to the short exciton diffusion length (short exciton lifetime) in organic solar cells, only excitons that are formed in close vicinity (about 10 nm) of the organic heterointerface can be separated into positive and negative charge carriers.

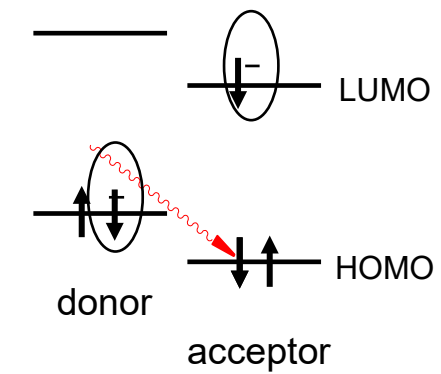
Depending on whether the electron donor or electron acceptor is photoexcited, reductive or oxidative charge transfer processes can occur if the frontier orbital levels are aligned in a favorable way.



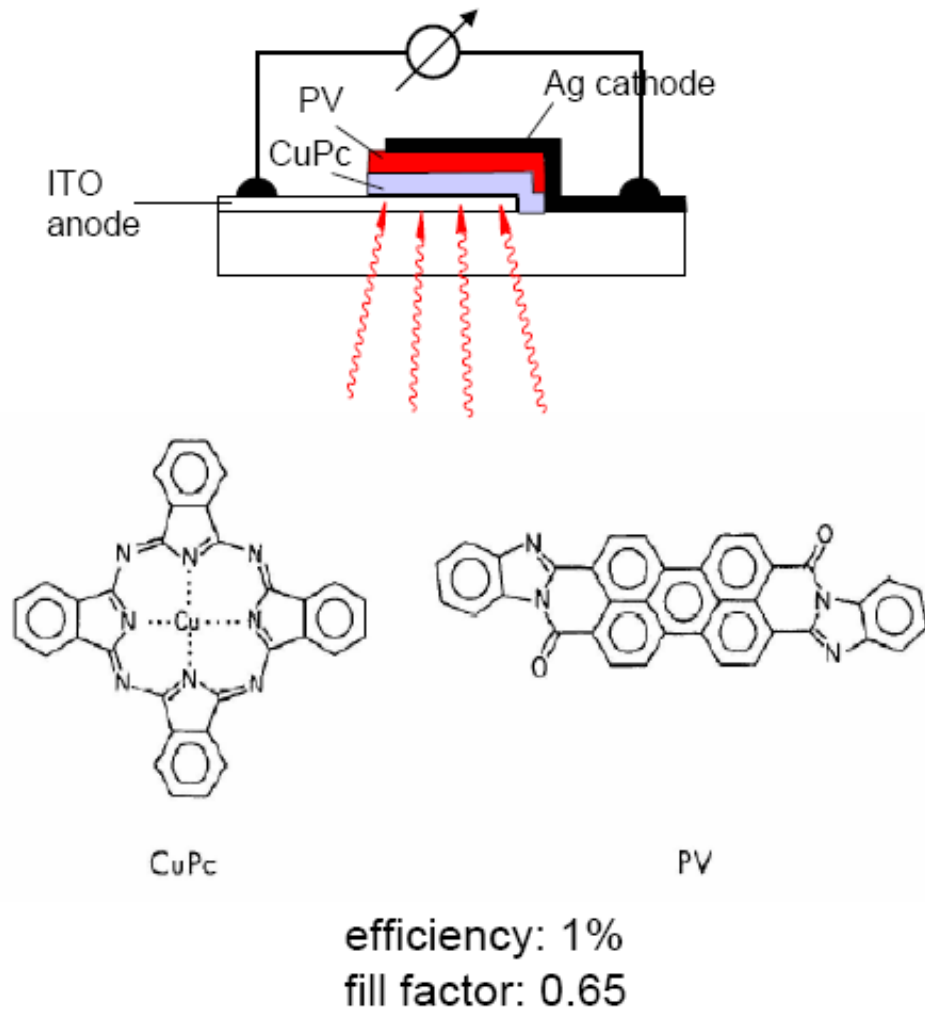
reductive electron transfer



oxidative electron transfer



Milestone I: Bilayer solar cells reach 1%



The spectral response comprises the spectral response of the chromophores of both donor and acceptor.

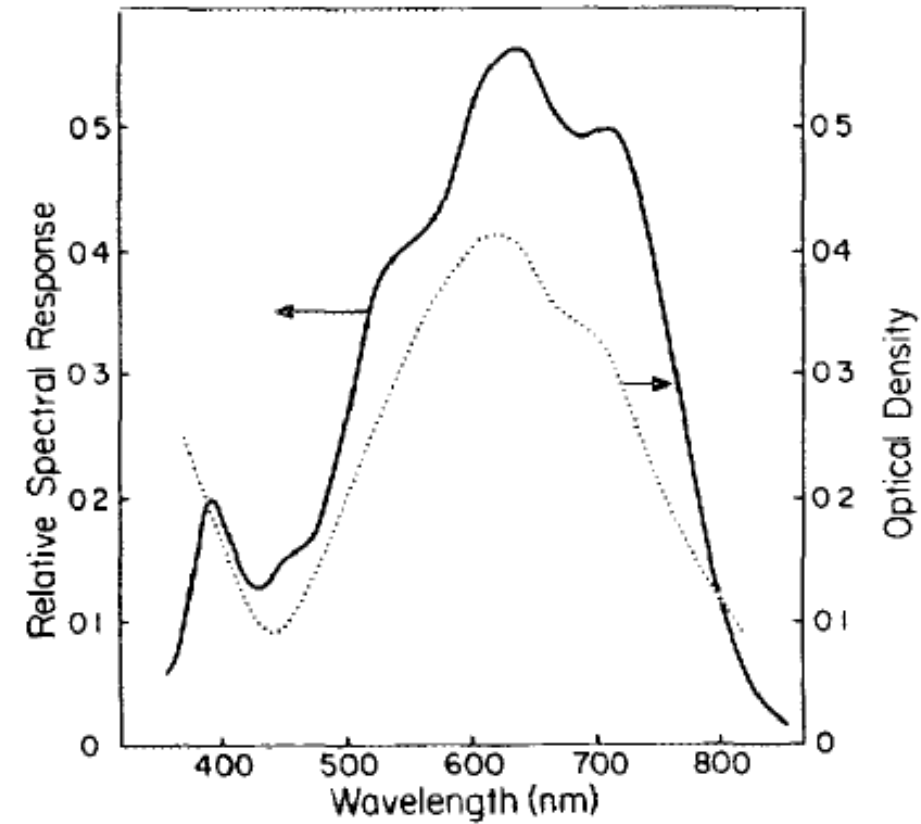
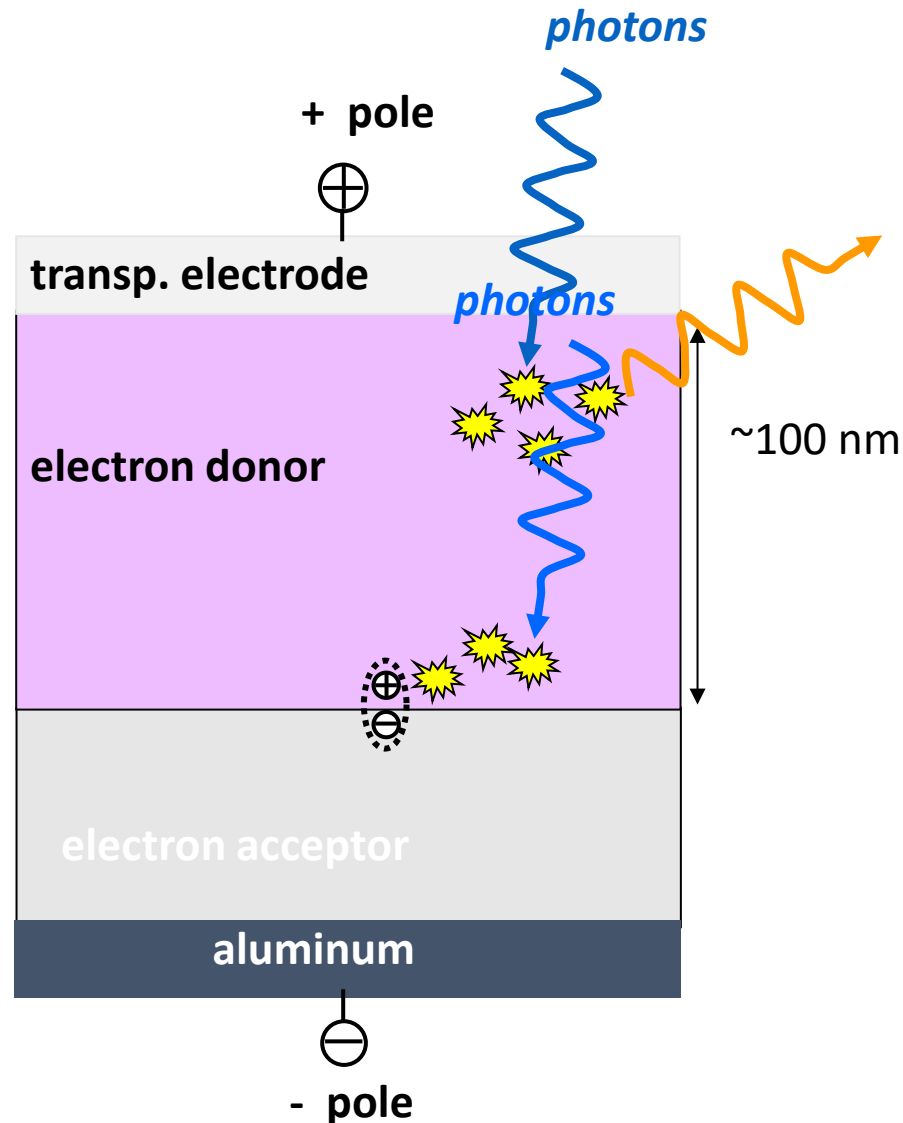


FIG. 2. Spectral response of an ITO/CuPc (250 Å)/PV(450 Å)/Ag cell and absorption spectrum of the CuPc/PV two-layer film.

Milestone II: The problem of the exciton diffusion length

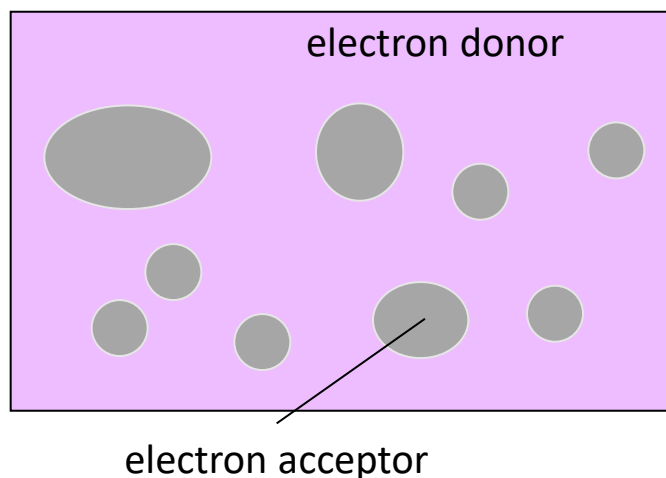


For an efficient solar cell it is primordial to absorb a large portion of the solar irradiation. Organic semiconductors benefit from very strong π - π^* transitions (absorption coefficient $\alpha \approx 10^5 \text{ cm}^{-1}$). As a consequence, films of 100 nm-200 nm are thick enough to harvest all the photons within the range of absorption. Advantageously, electrons and holes do not have to travel long distances and can be extracted with high efficiency.

Upon absorption, excited states are formed (excitons) which have a lifetime of about 1 ns. During this lifetime, they diffuse within the solid. Typically the diffusion length is about 5-20 nm. This condition brings a difficulty, namely that excitons that are excited far from the donor-acceptor interface will not be dissociated at the heterointerface. Ideally, a comb-like nanostructure between donor and acceptor should be fabricated.

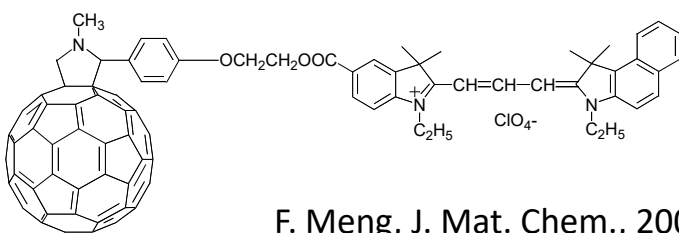
Much of the conceptual research work leading to higher efficiency devices has therefore focused on the problem of short exciton diffusion length.

What about blending of donor and acceptor?

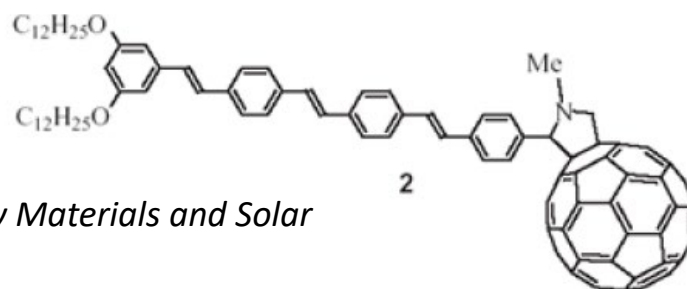


If the blend results in phase segregation, of isolated domains, charge transport of one of the species (electrons for the figure on the left) is trapped and extraction is not efficient. It has therefore been tried to synthesize tethered donor-acceptor diads such that no phase separation can occur. Such molecules are shown below for donor-acceptor dimers and polymers incorporating the donor in the main chain and the acceptor in the side chain (so-called double cable polymers).

Both approaches suffer from the fact that charge recombination is enhanced in such films. The advantage is the fact that charge generation is extremely efficient.

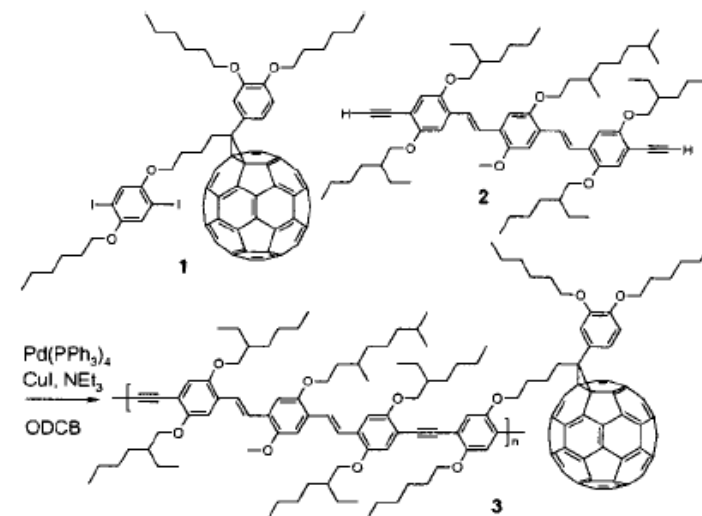


F. Meng, J. Mat. Chem., 2005, 15,979-986 979



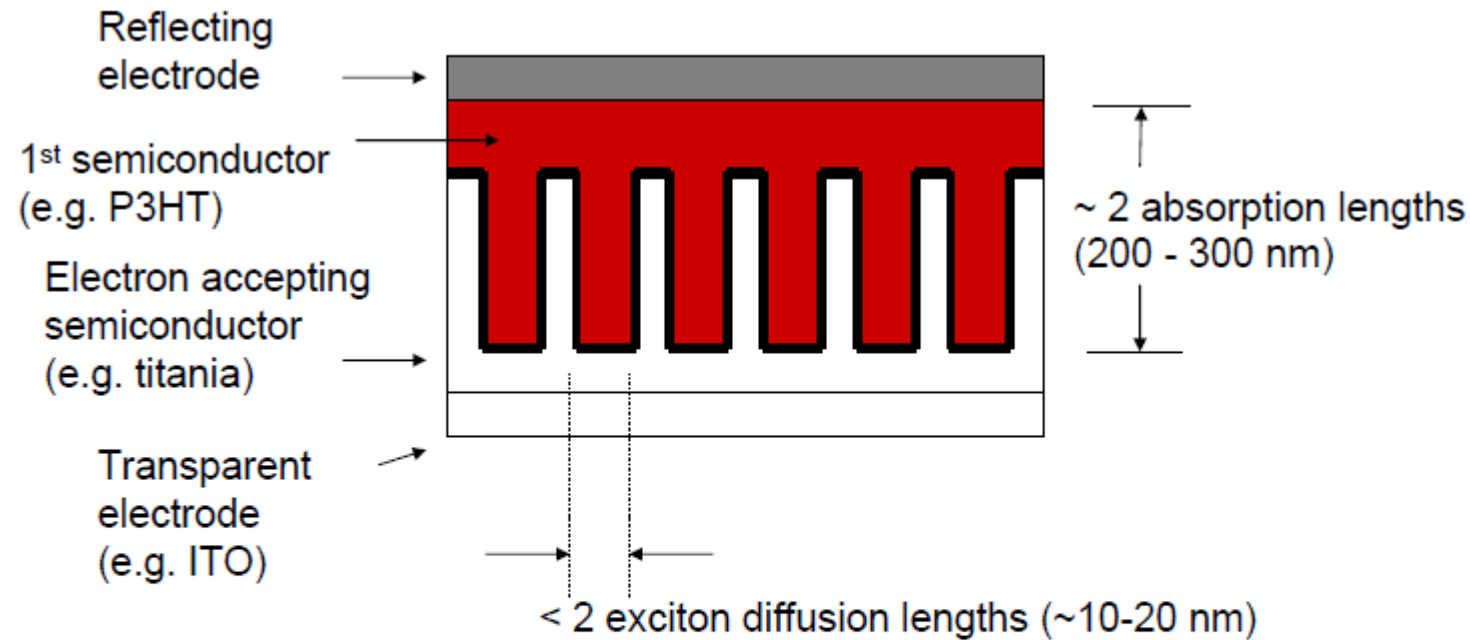
Nierengarten et al., *Solar Energy Materials and Solar Cells*, **83** (2004), 187-199

"double cable polymers"



Ramos et al., *JACS*, 123 (2001), 6714.

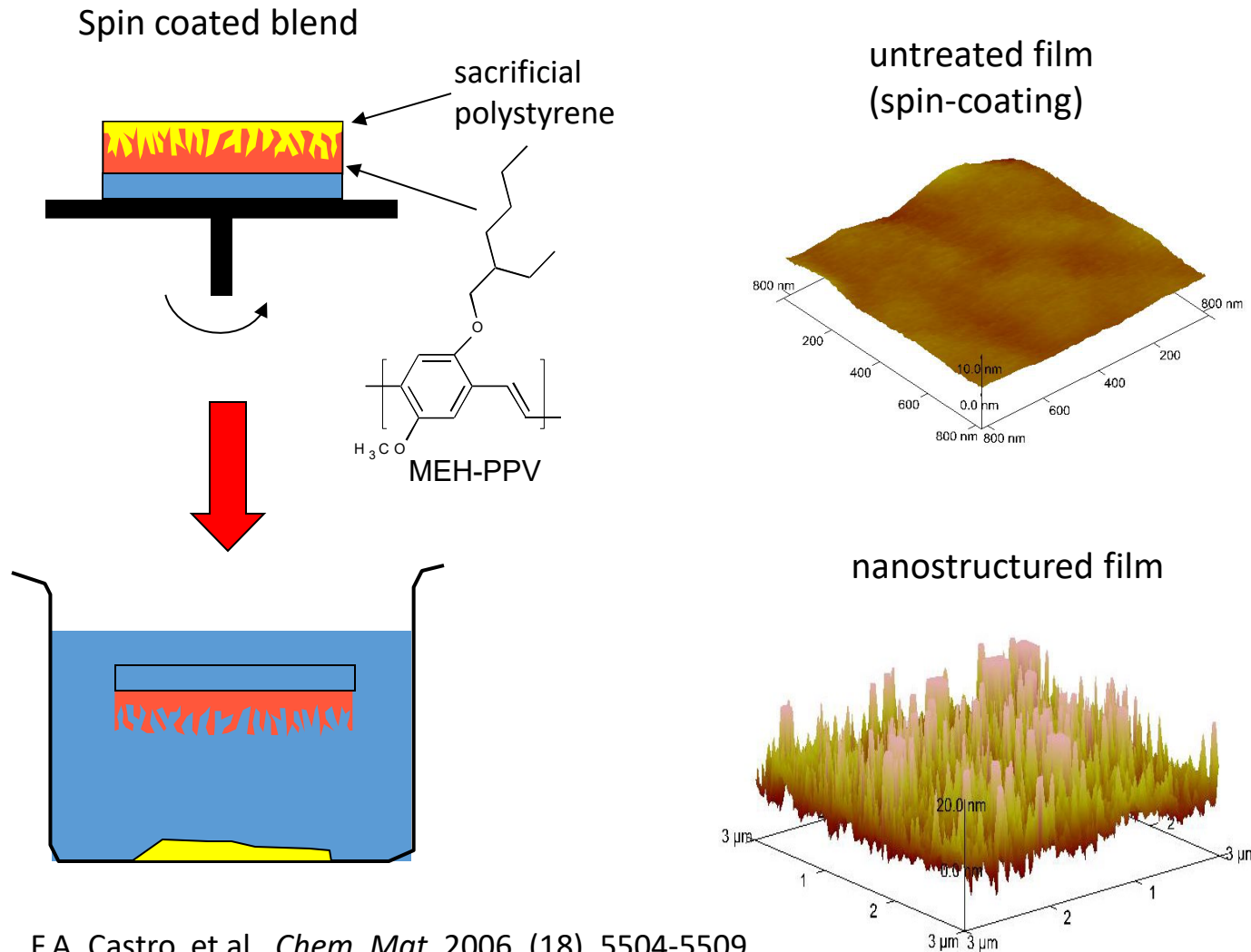
Ordered bulk heterojunction



- Almost all excitons can be split
- No deadends
- Polymer chains can be aligned

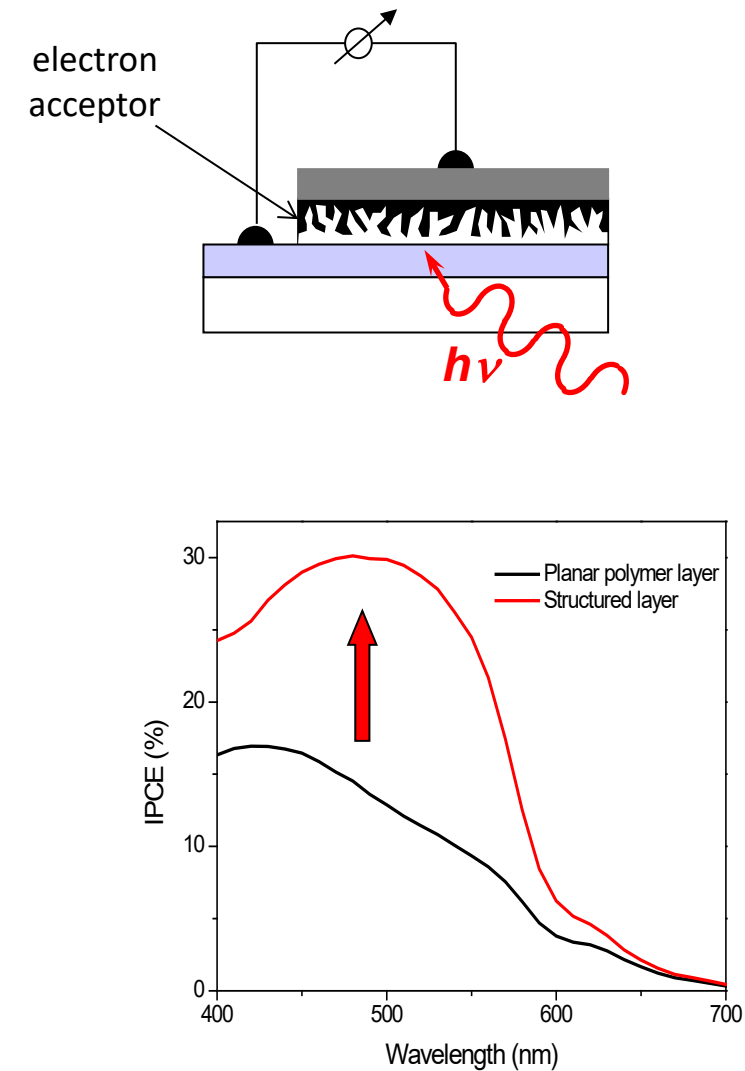
- Easy to model
- Semiconductors can be changed without changing the geometry.

Fabricating nanostructured heterojunctions

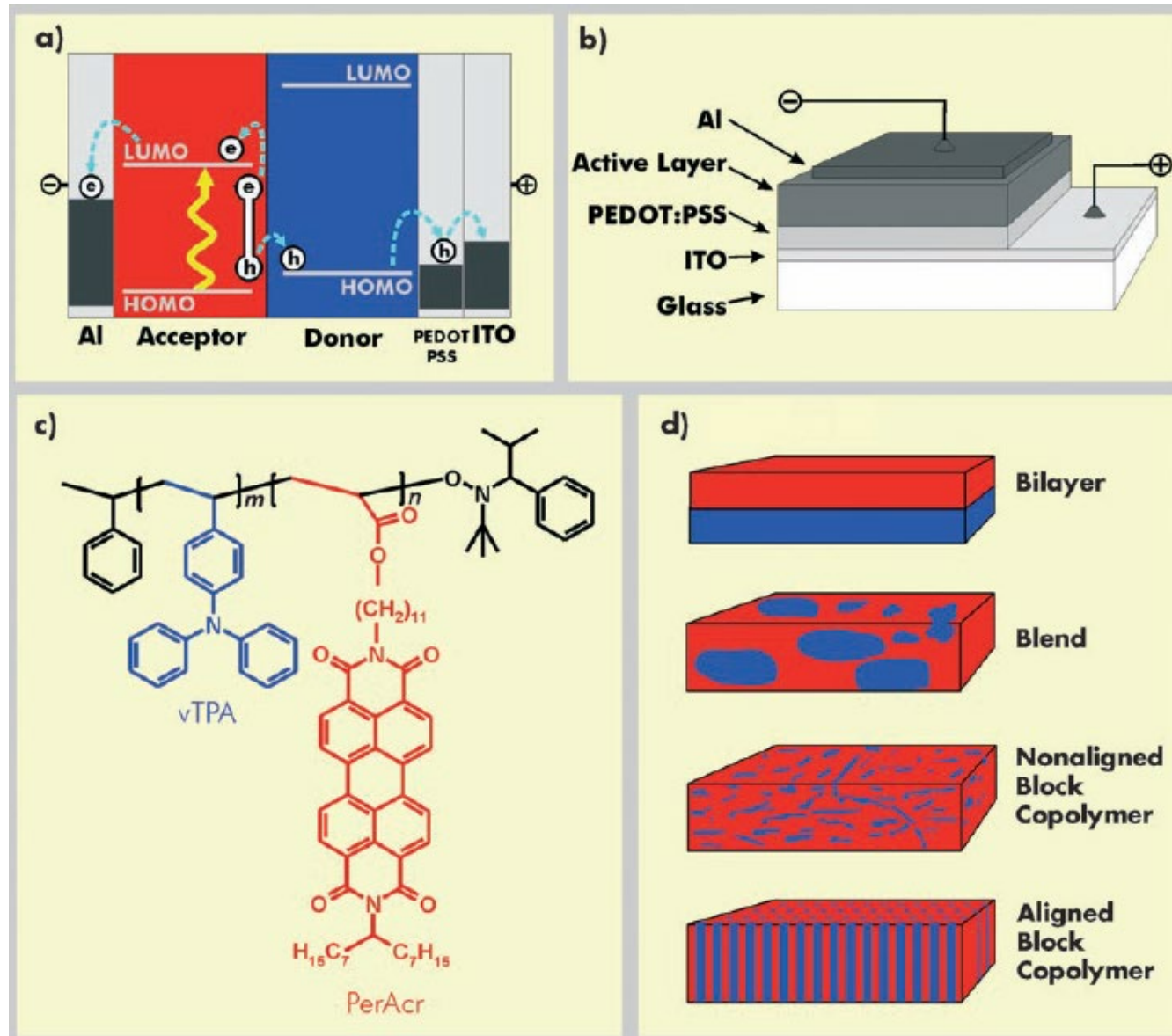


F.A. Castro, et al., *Chem. Mat.* 2006, (18), 5504-5509.

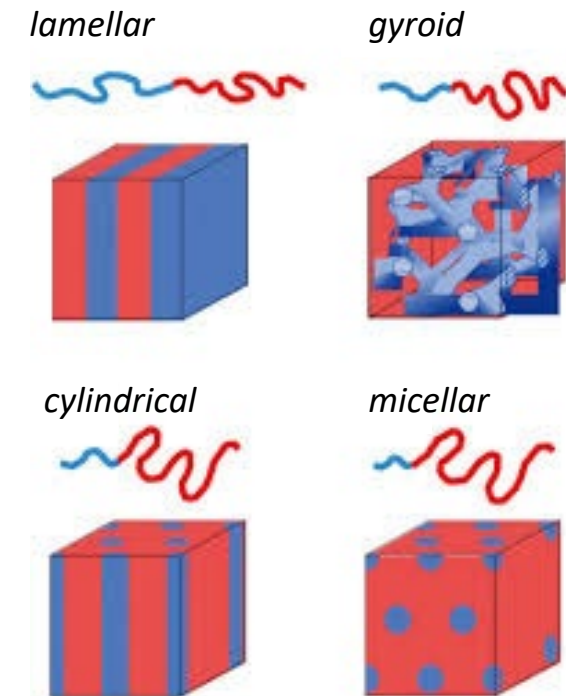
F.A. Castro, C.F.O. Graeff, J. Heier, R. Hany, *Polymer*, 48, (2007), 2380-2386



Designing film morphology at the molecular level: block copolymers

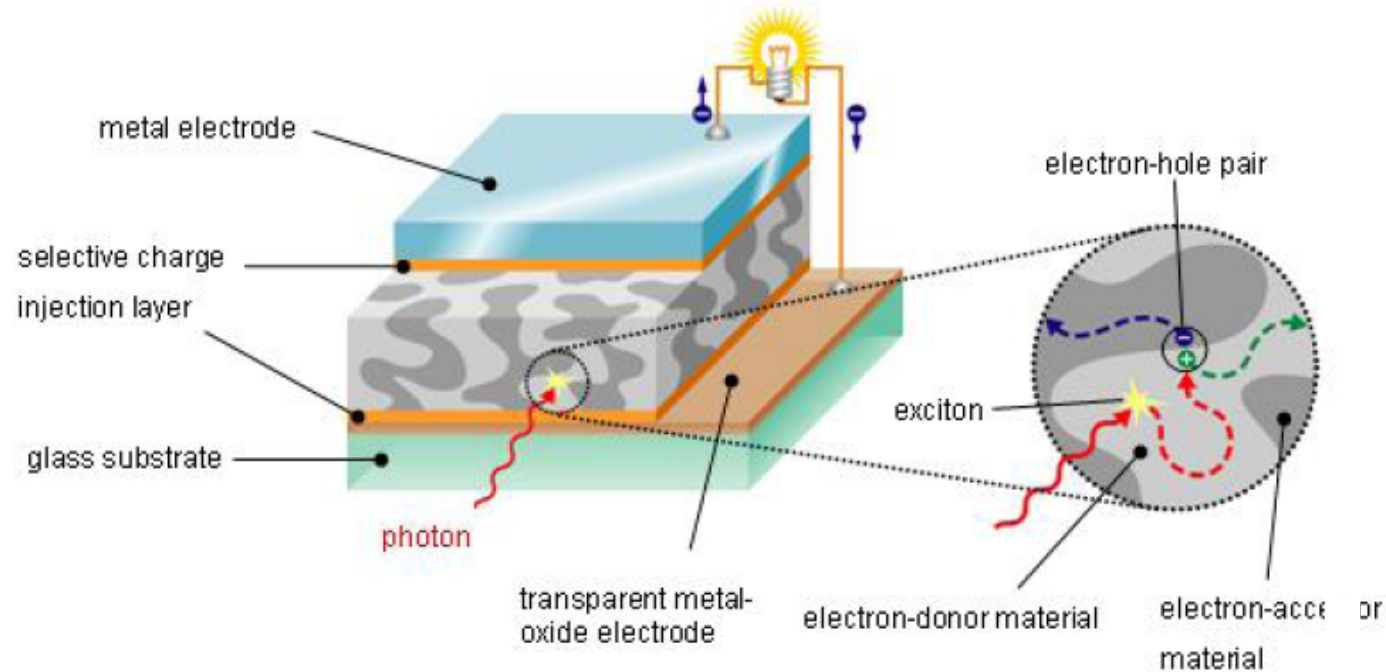


Albeit very appealing, the concept of block copolymers has so far provided power conversion efficiencies below 10%. The reason is not very clear, but it could be related to the difficulty to produce well aligned structures. Also the possibility to use gyroid structures has so far been difficult to achieve.

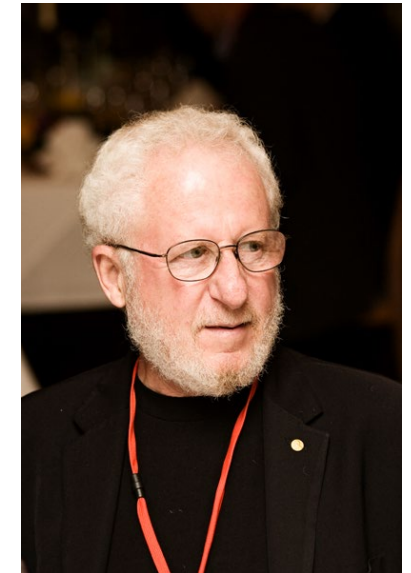


S. M. Lindner et al., Angew. Chem. Int. Ed. 2006, 45, 3364–3368

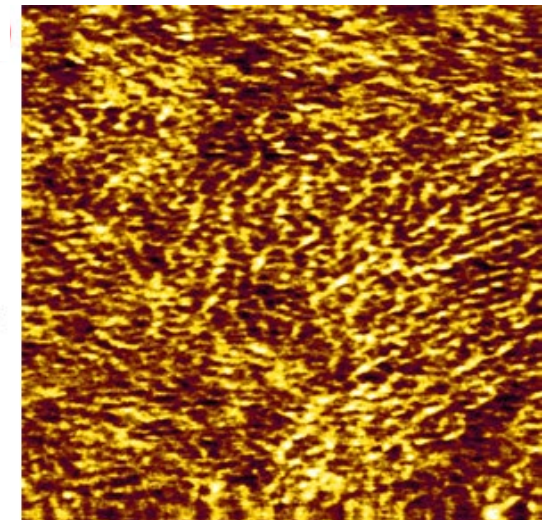
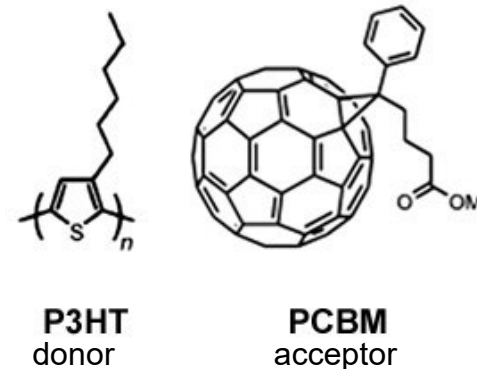
Bulk heterojunction solar cells by blending donor and acceptors: the art of fine-tuning morphology



Allan Heeger, UCSB
bulk-heterojunction
using conj. polym.

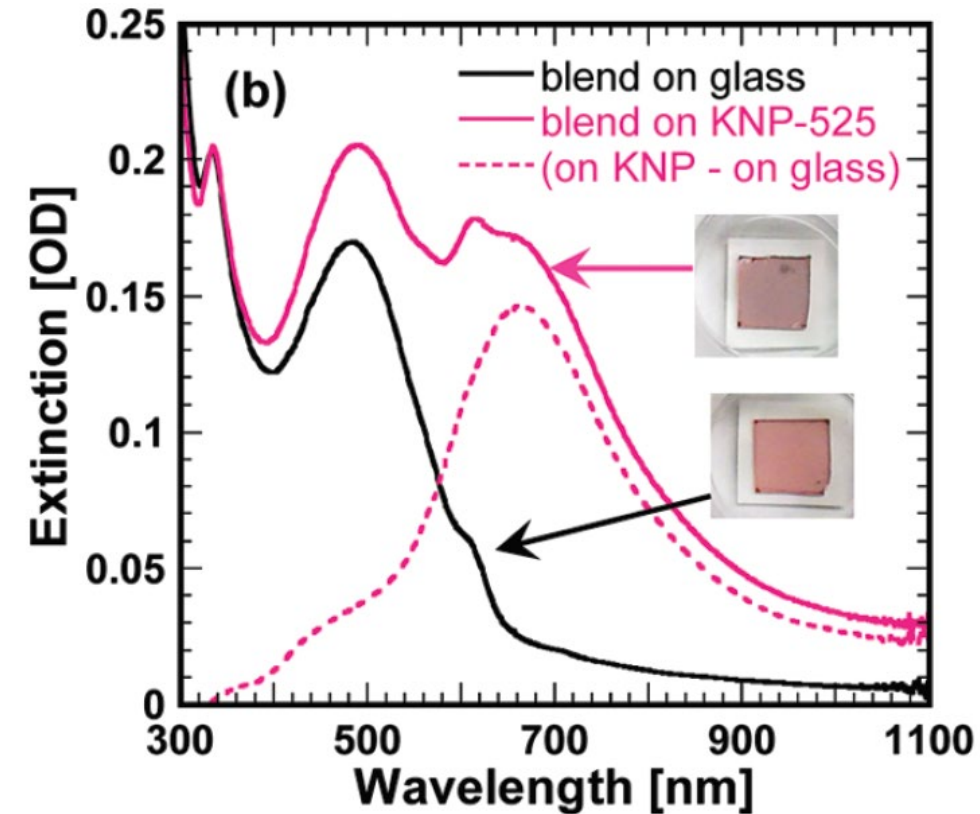
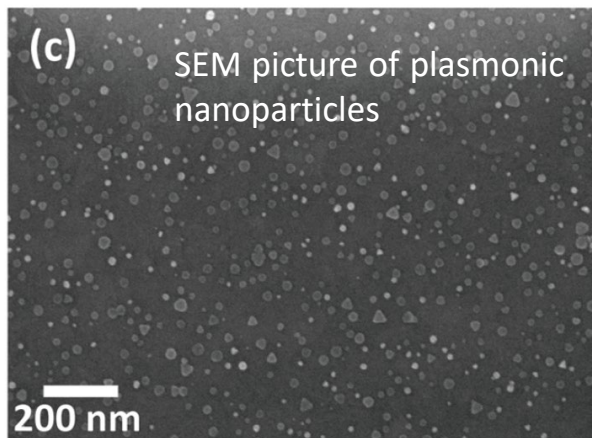
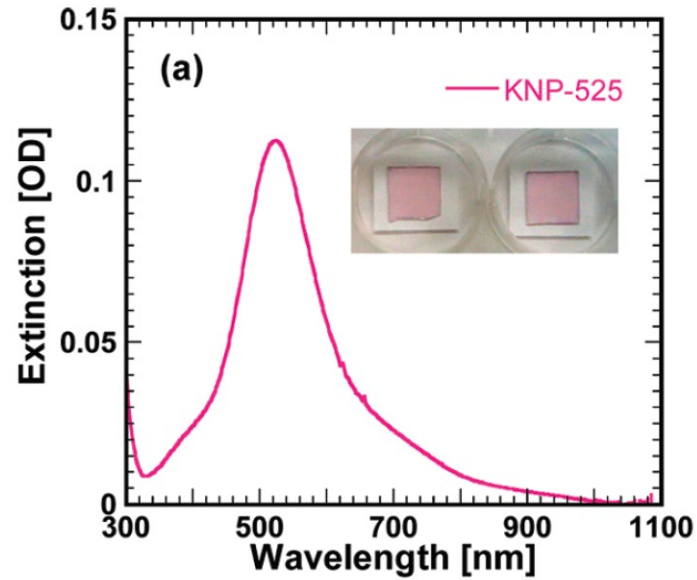


P3HT and PCBM today are reference donor-acceptor materials for organic solar cells deposited from solution. Power conversion **efficiency of 4%** in this system is limited by the limited width of the absorption spectrum of P3HT (onset at about 630 nm). Therefore much effort has been spent on “pushing” absorption to the NIR domain. Some other strategies have employed plasmonic light scattering by metallic nanoparticles.



Absorption enhancement using plasmonic nanoparticles

Extinction coefficient of nano-prism particles on glass slides (top)

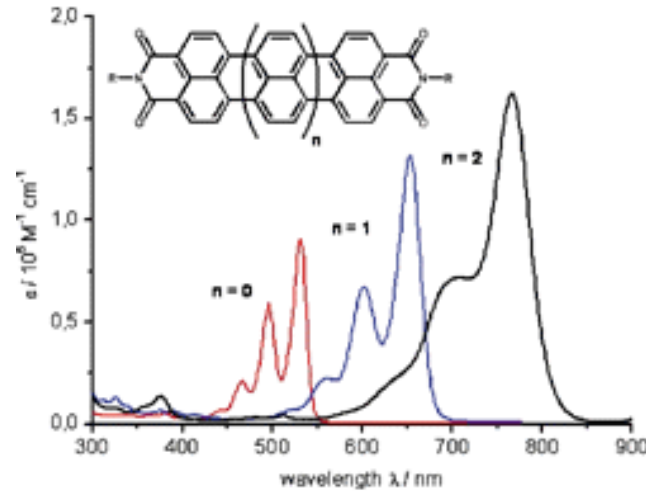


Extinction spectra of 35 nm thick P3HT/PCBM blend film on glass (solid black line) and on silver nano-prisms (solid pink line). The dotted pink line is the difference between the extinction spectra of the polymer blend on bare glass and the polymer blend on the nano-prisms. With the polymer coating, the nano-prism LSPR resonances red shift by ~ 140 nm. This red shift is primarily attributed to the change in refractive index sensed by the nano-prisms in going from air ($n = 1$) to polymer film on top ($n \sim 1.7$).

A.P. Kulkarni et. al., DOI: 10.1021/nl100615e, *Nano Lett.* **2010**, 10, 1501–1505

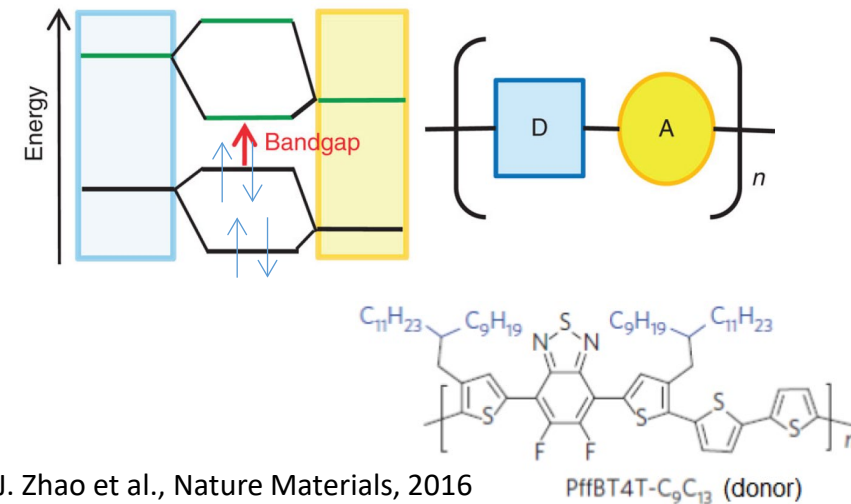
Milestone III: Developing molecules absorbing in the near infrared (NIR)

Large *p*-conjugated systems (graphene, rylene dyes etc.)



Herrmann et al., Chemistry Letters Vol.35, No.9 (2006)

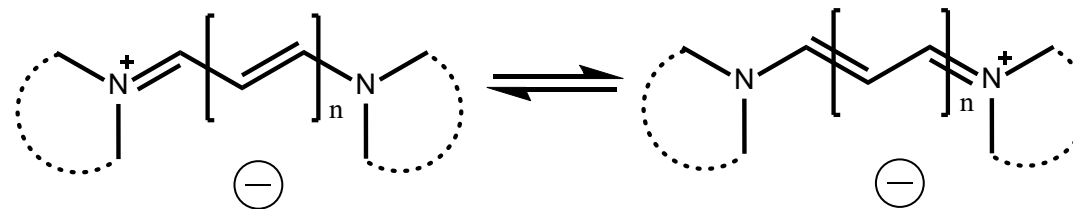
Donor-acceptor CT motives



J. Zhao et al., Nature Materials, 2016

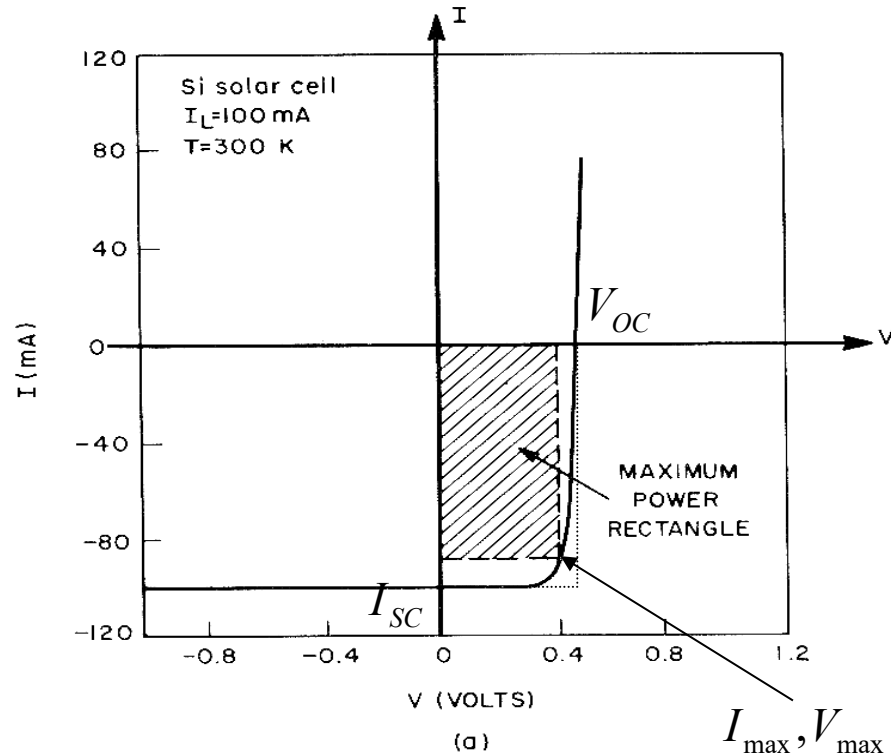
PffBT4T-C₉C₁₃ (donor)

Cyanine dyes (Brooker cations)



- odd number of linear vinylene units, fully conjugated system flanked by N atoms
- "cyanine limit" : 100 nm red shift per vinylene unit
- counterion for tuning material properties

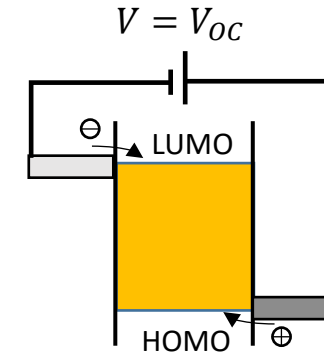
Short circuit current I_{SC} , open circuit voltage V_{OC} , power conversion efficiency η_{PCE} , and external quantum efficiency EQE (sometimes also called incident photon to converted electron or IPCE) are defined below:



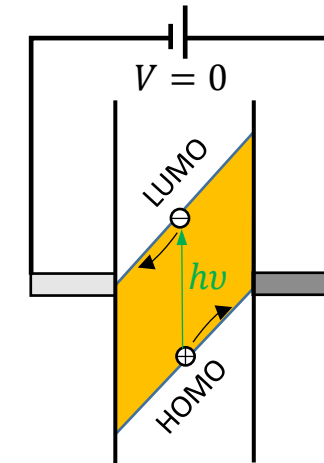
Power conversion efficiency (η_{PCE}):

$$\eta_{PCE} = \frac{P_{electric}^{out}}{P_{photons}^{in}} = \frac{V_{max} I_{max}}{P_{photons}^{in}} = \frac{FF \cdot V_{OC} I_{SC}}{P_{photons}^{in}}$$

Open circuit condition:



Short circuit condition:
(the current is negative, i.e. is opposite to the forward direction of the diode):

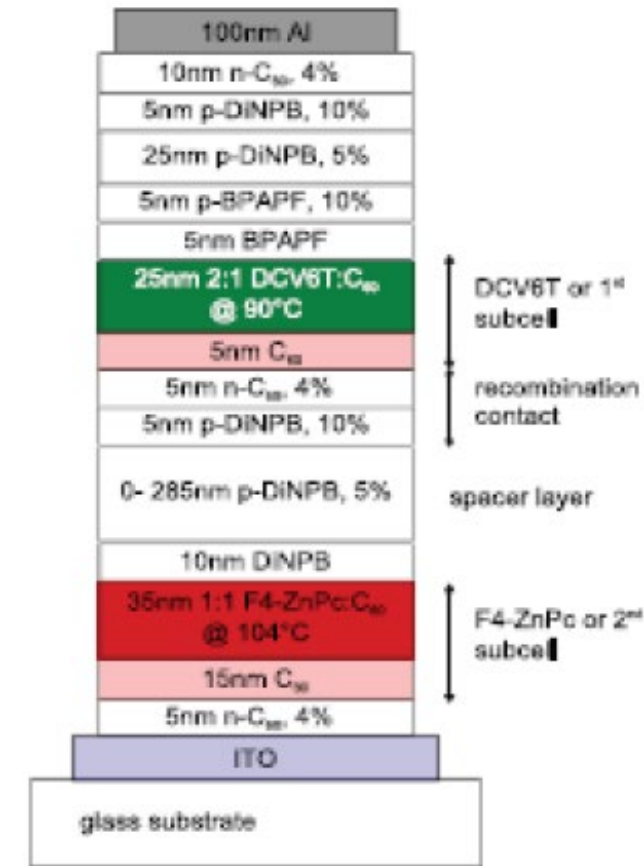
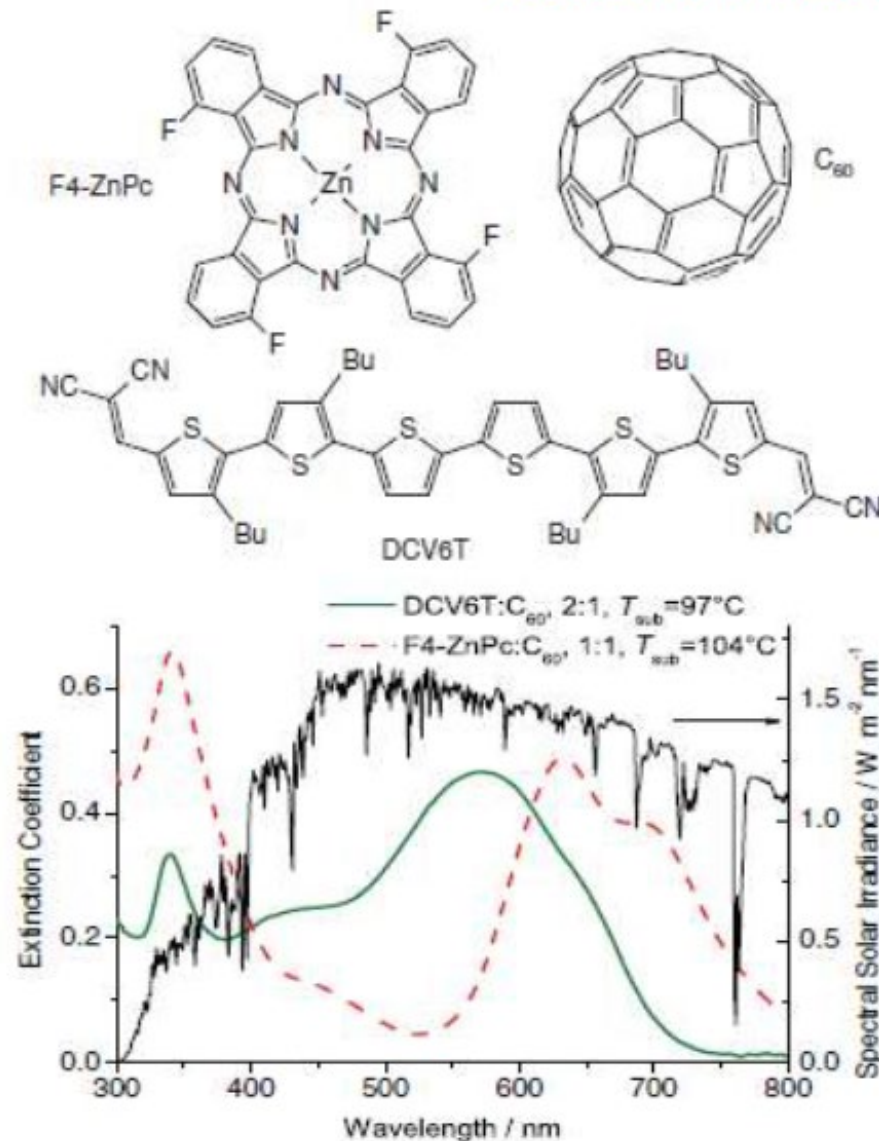


External quantum efficiency EQE :

$$EQE = \frac{\text{number of generated electrons}}{\text{number of incident photons}} = \frac{I_{SC}(\lambda) / |e|}{P_{photons}^{in}(\lambda) \lambda / hc} = \frac{I_{SC}(\lambda) \cdot hc}{P_{photons}^{in}(\lambda) \cdot \lambda \cdot e}$$

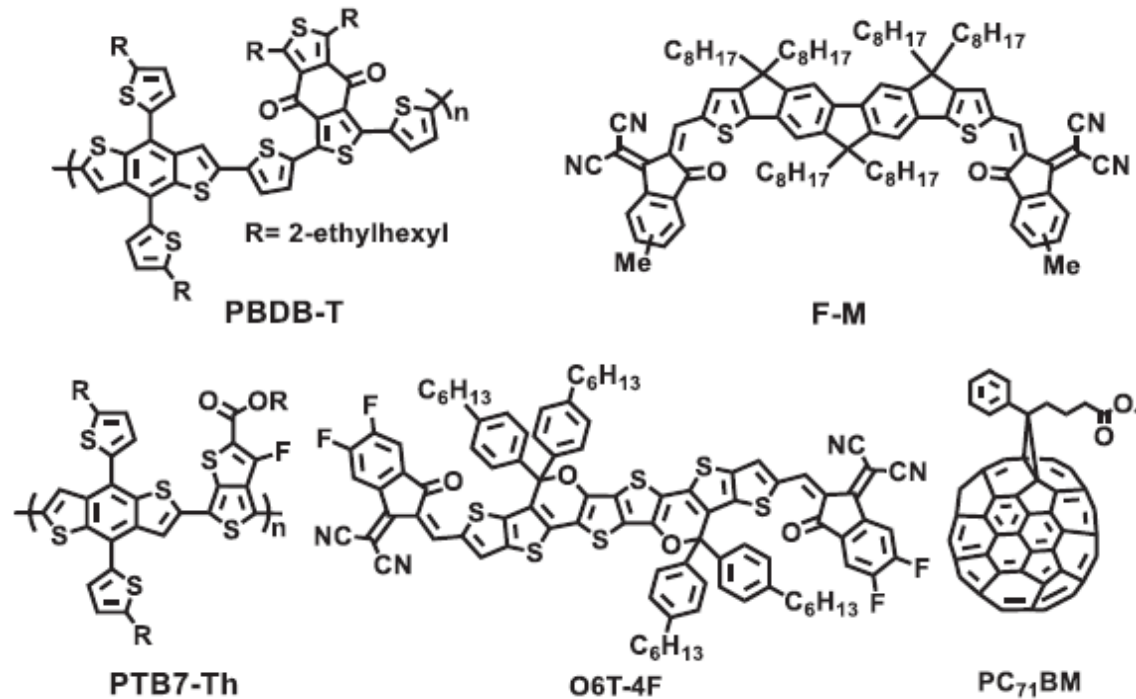
13.2 % 2016 world record for small molecule multi-junction solar cells (Heliatek press release)

Closest Published Info. – 6.1%



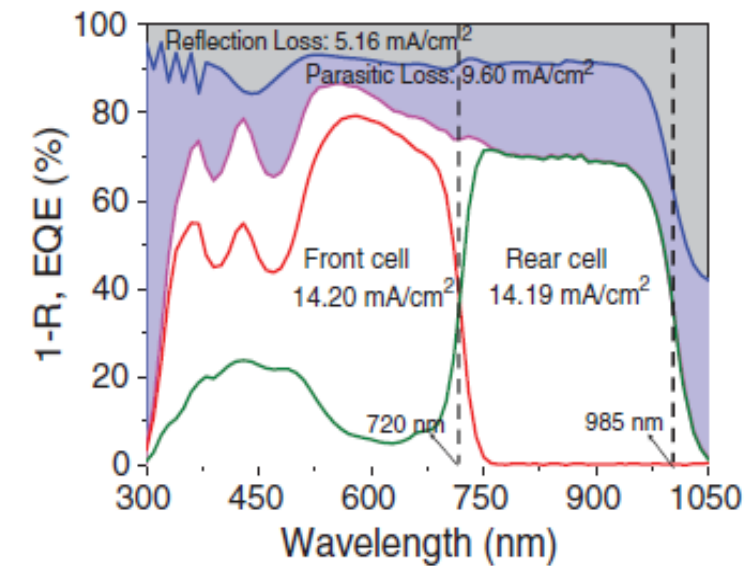
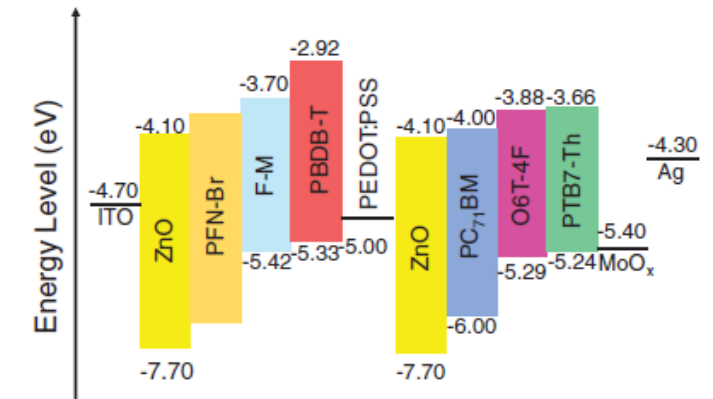
Adv. Funct. Mater. 2011, 21, 3019

Organic and solution-processed tandem solar cells with 17.3% record efficiency

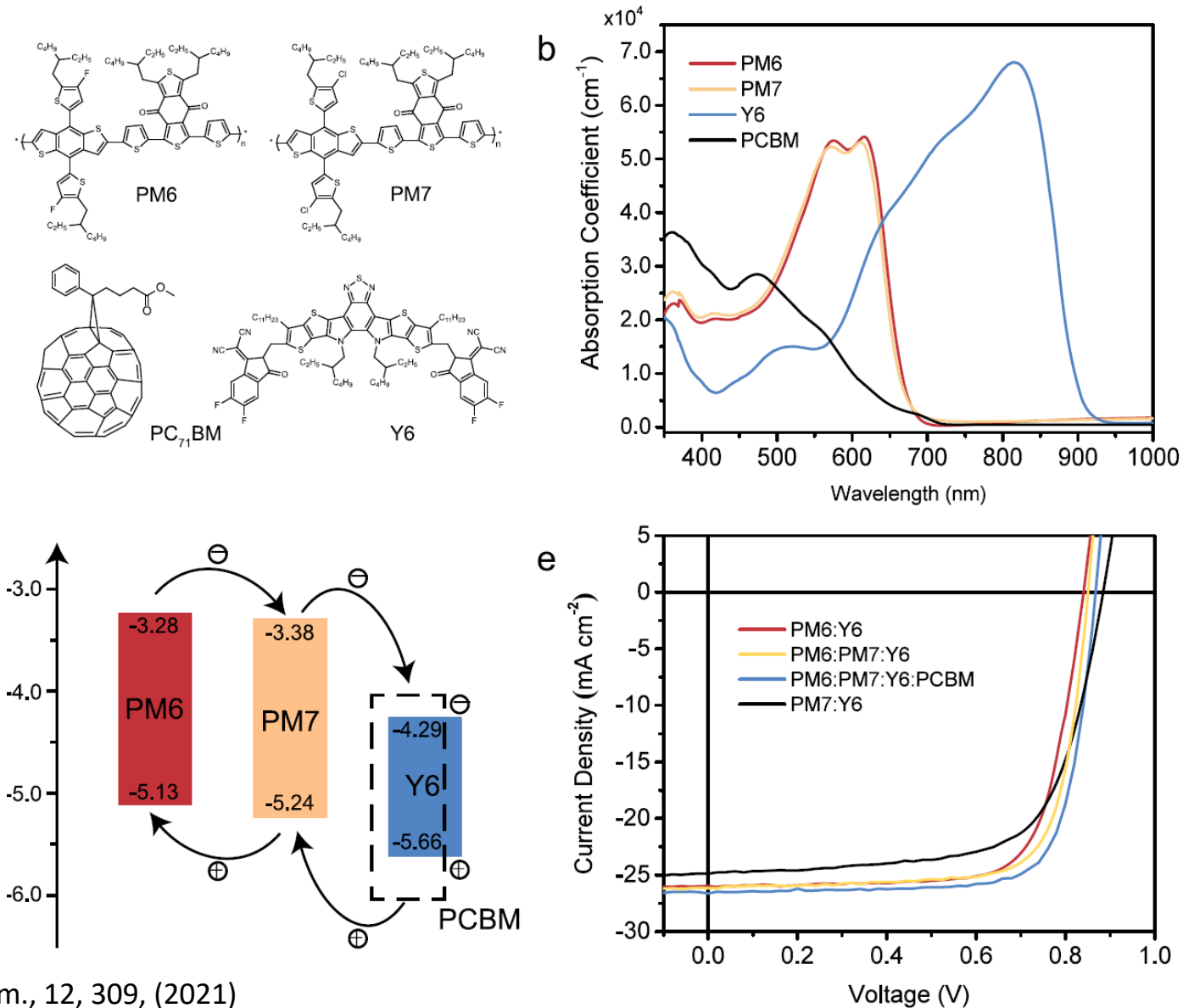


- Broad band absorption
- Perfect current matching
- Optical optimization

L. Meng et al., Science 361, 1094–1098 (2018)

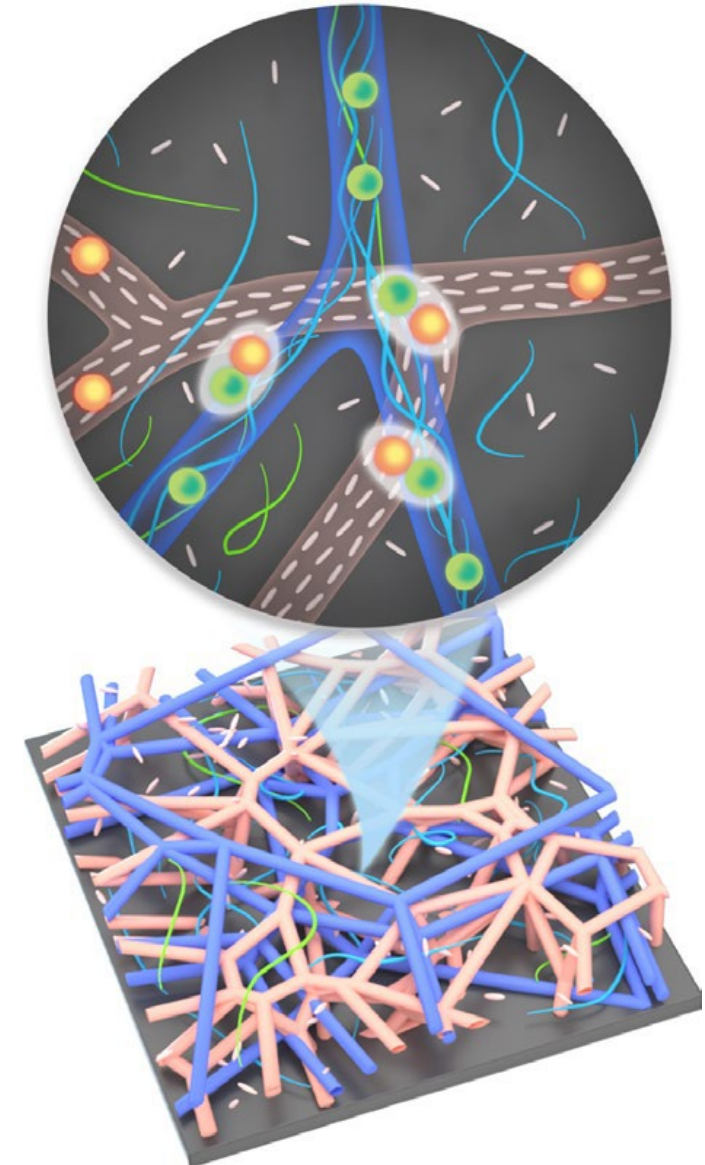
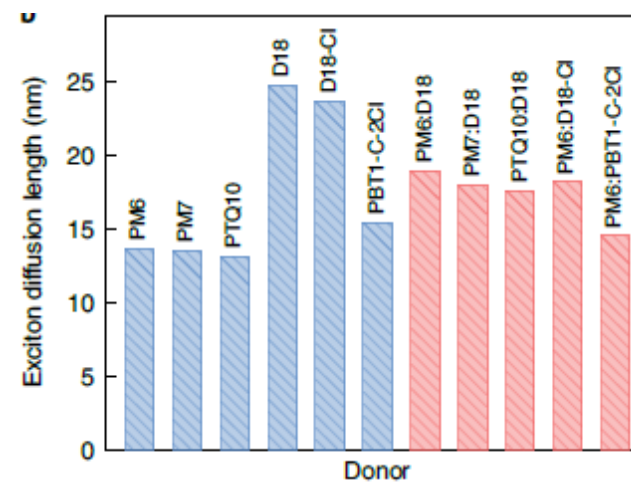
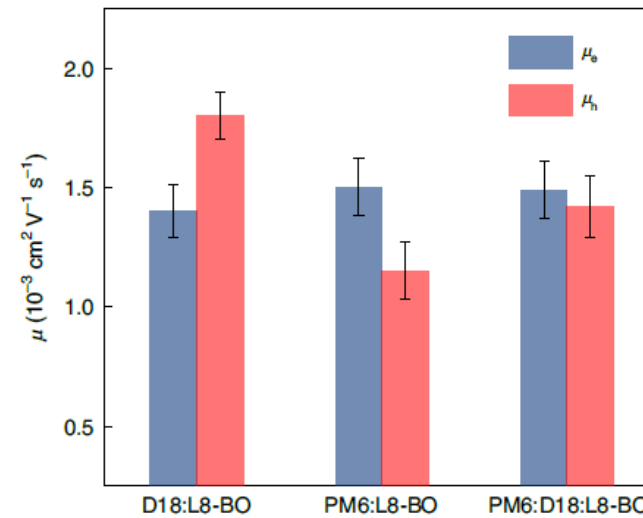
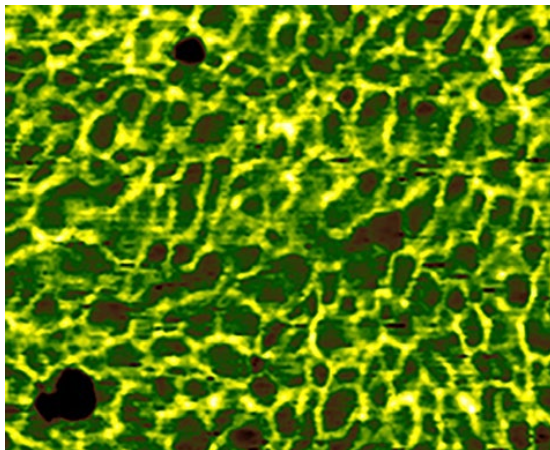
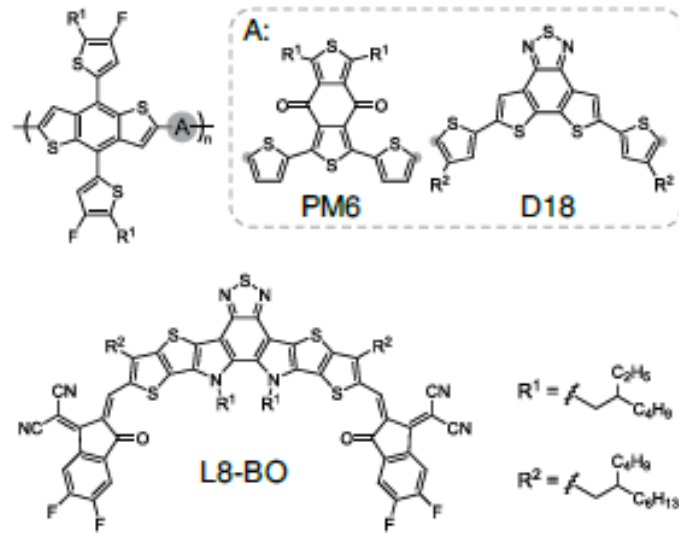


18% efficiency record using quaternary blends for the donor-acceptor heterostructure

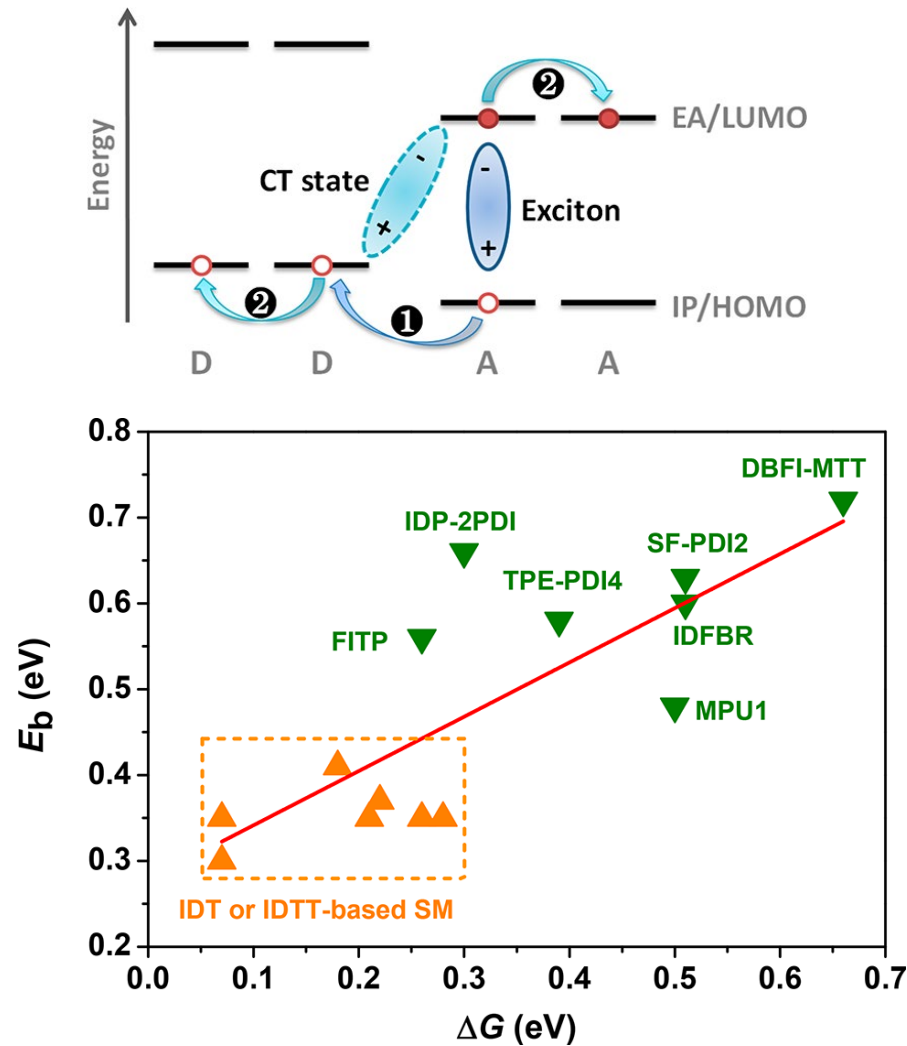


M. Zhang et al, Nature Comm., 12, 309, (2021)

19.3 % efficiency record using ternary blends for the donor-acceptor heterostructure



Exciton dissociation in non-fullerene acceptors



ΔG is the (experimental) driving force for hole transfer
 E_b is the exciton binding energy

