Organic light-emitting diodes

Basic Device Physics and Materials

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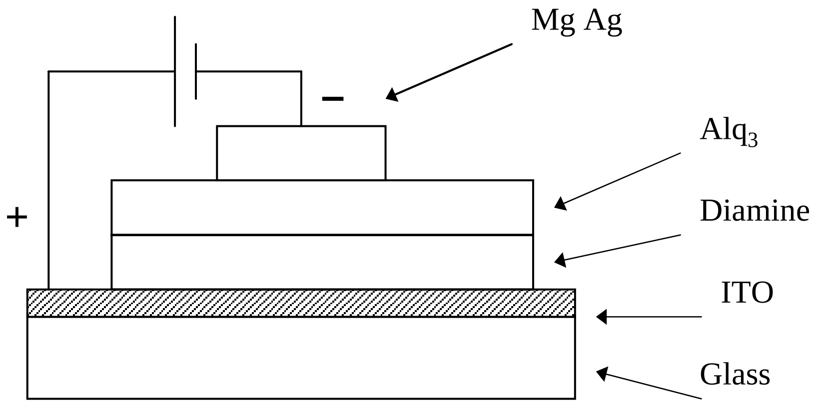
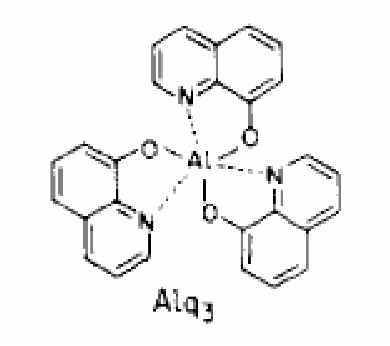
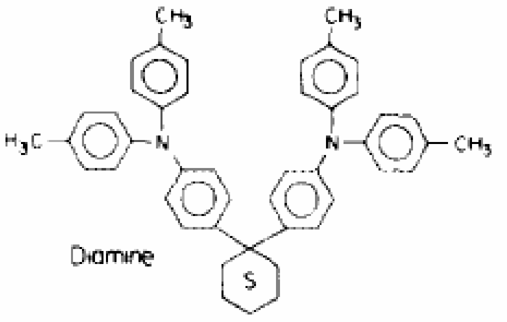
Device structure of OLEDs



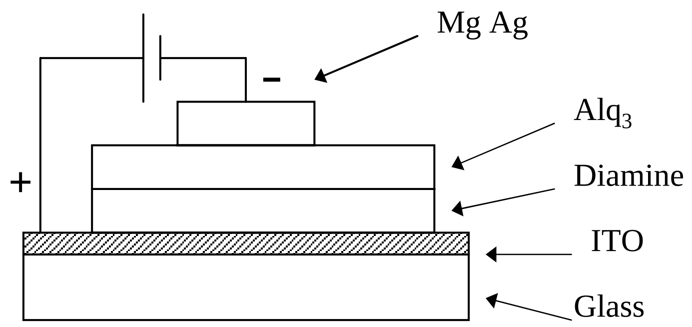


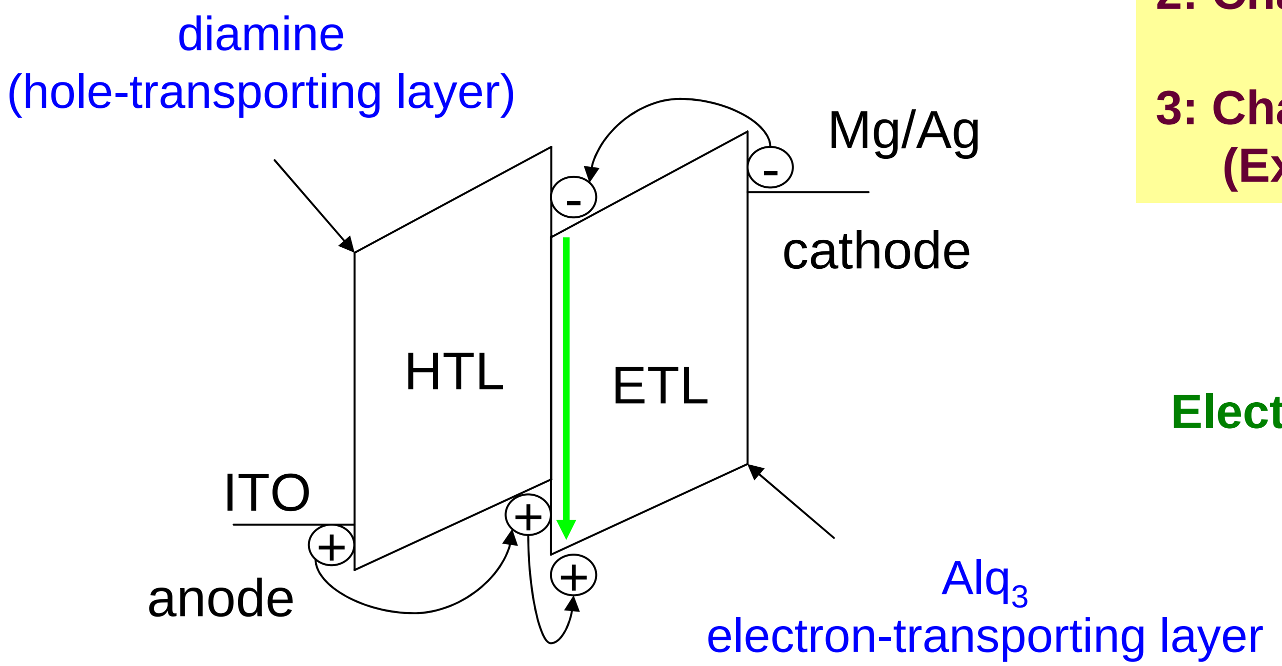


Devices were fabricated by thermal evaporation

Drive voltage ~5V
QE: ~1%; 3 cd/A (green)
Fast response time (<1 μsec)

Operating mechanism of OLEDs





Mechanism involves:

1: Charge injection

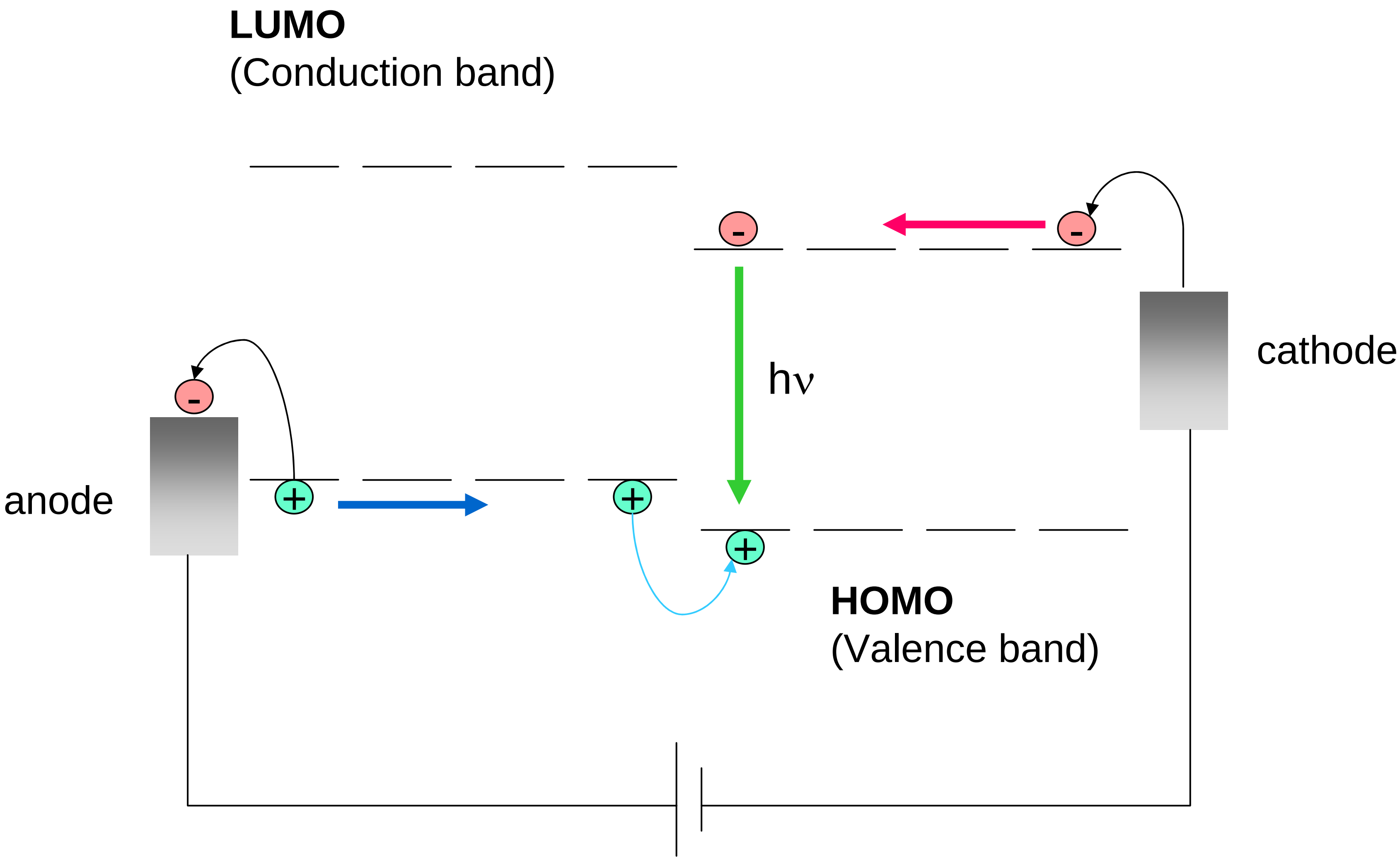
2: Charge transport

3: Charge recombination (Exciton formation)

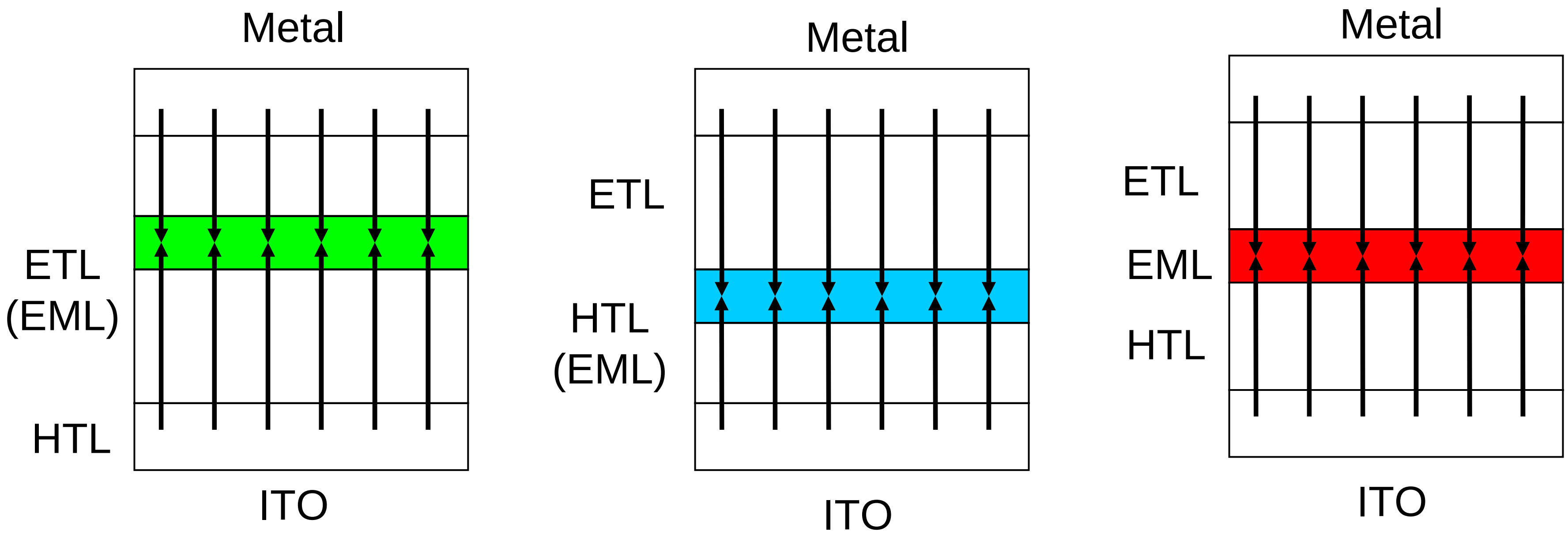
Electrical field: >10^5 V/cm

100 nm; @~1V

Operating mechanism of OLEDs

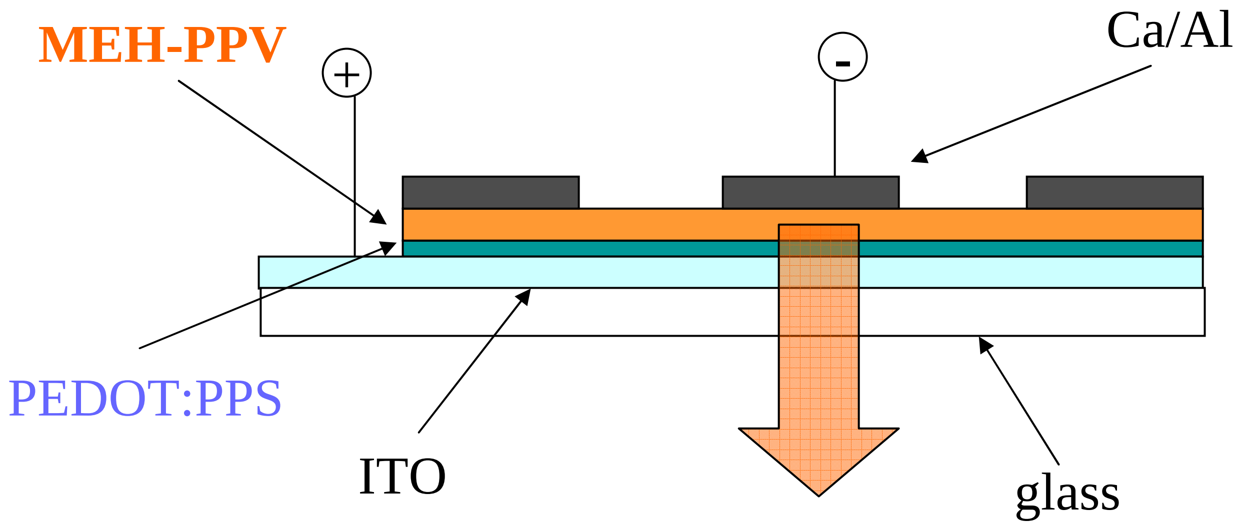


Typical multilayer-device structures

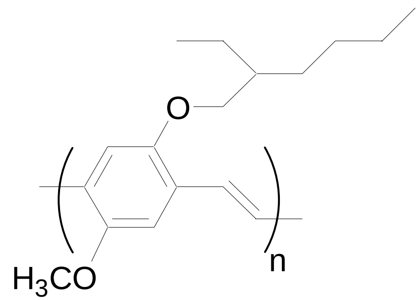


ETL, electron-transport layer
EML, emissive layer
HTL, hole-transport layer

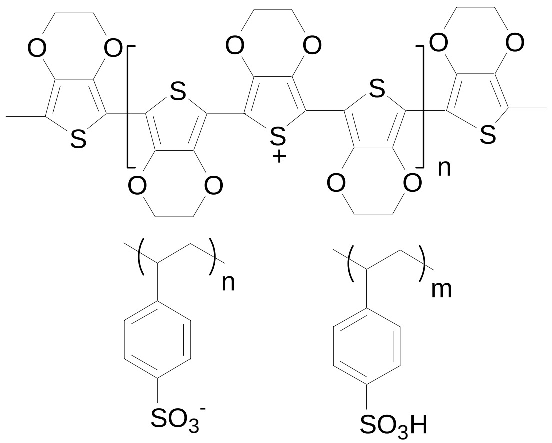
Operating mechanism of PLEDs



MEH-PPV



PEDOT:PPS



Devices were fabricated by spin-coating
Single emissive layer was used

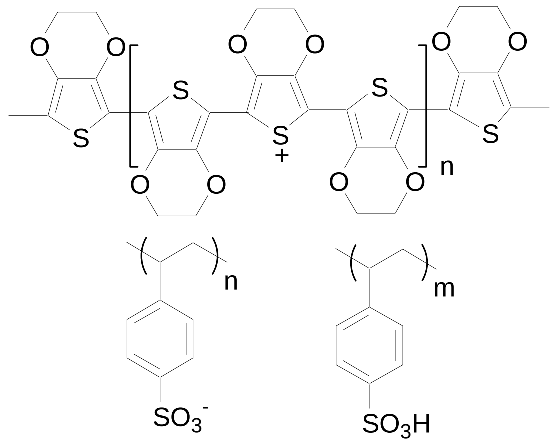
What is PEDOT:PSS?

PEDOT:PSS is a hole-transporting conductive polymer
Deposited from an aqueous suspension

ρ ~ 1000 to 100000 Ω-cm

Work function ~ 5.0±0.2 eV

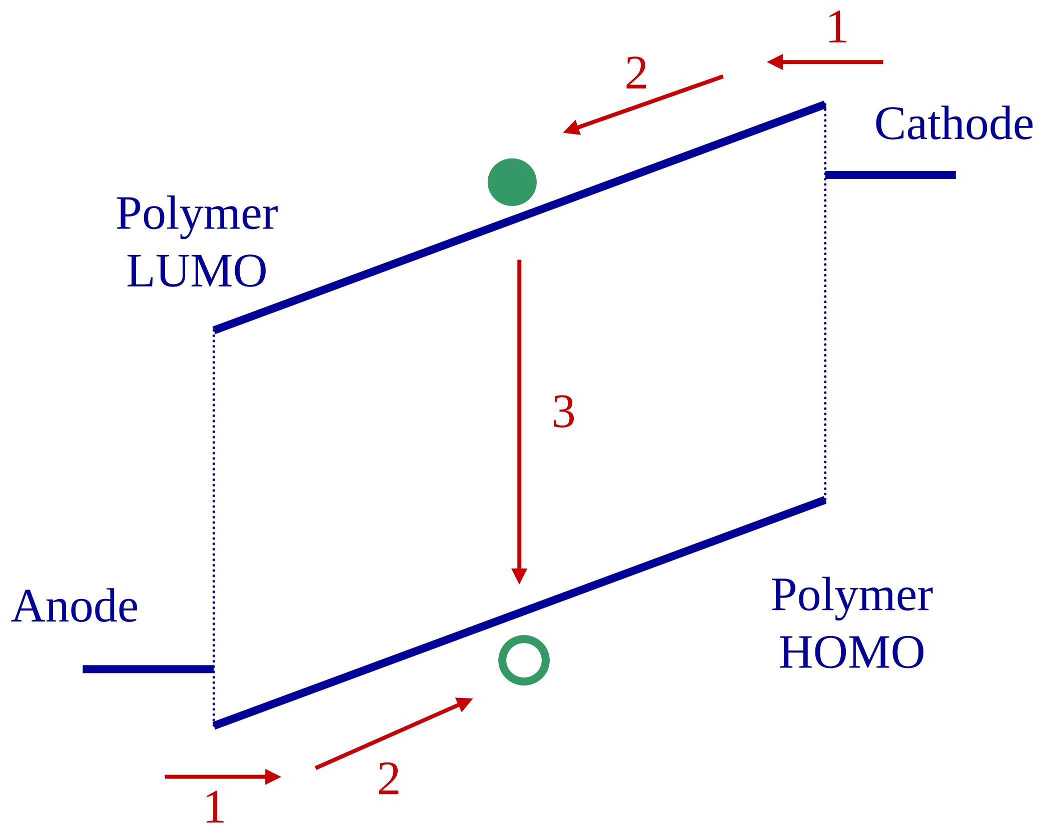
PEDOT:PPS



ITO work function depends on the surface treatment
ITO surface is often full of spikes

PEDOT:PSS (~ 100 nm) both planarizes the surface
and stablizes the work function of the anode of the PLEDs
It is one of the keys to reproducible devices

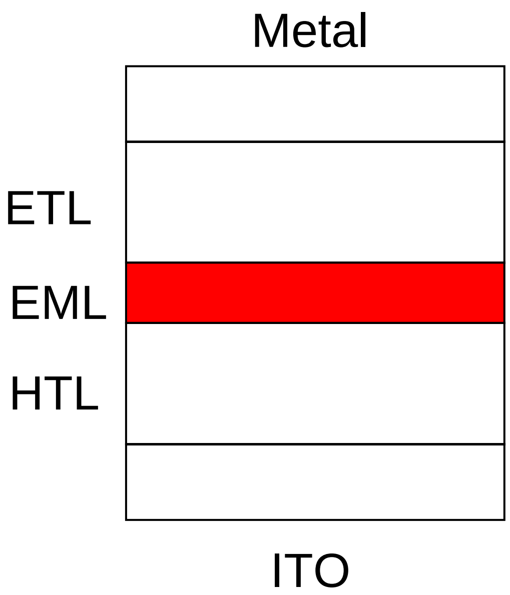
Single layer organic EL device

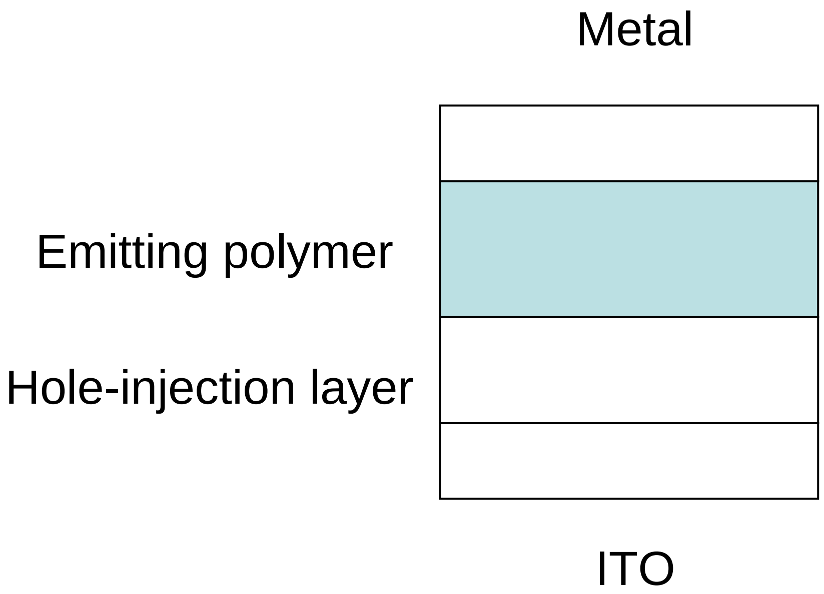


Very common for PLEDs

The material should be "bi-polar"

Small molecule and Polymer OLEDs



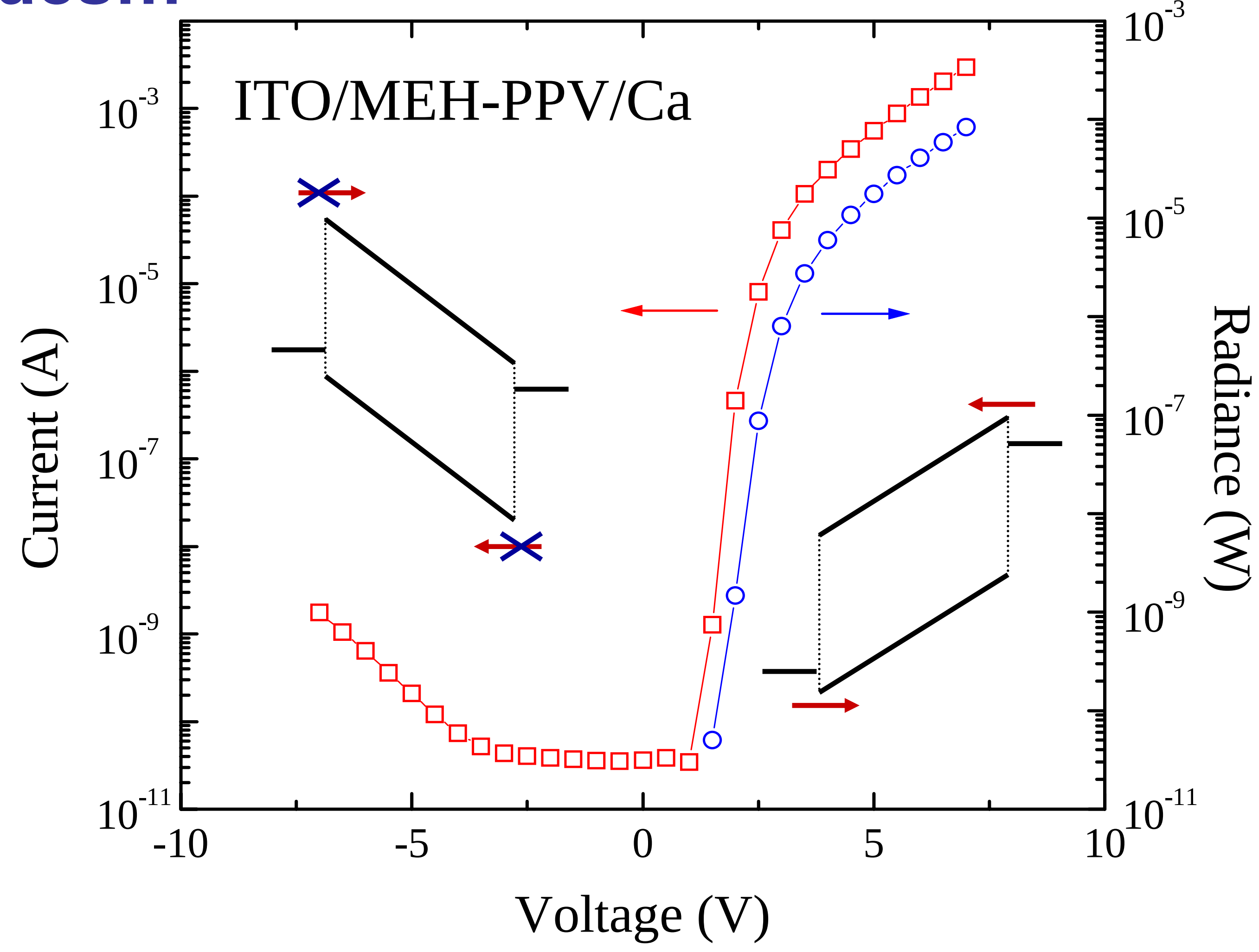


smOLEDs:
Evaporation of a multilayer stack of small organic molecules
(Mw ~ several 100)

PLEDs:
Spincoating/inkjet printing of polymers
(Mw ~ 50,000 – 500,000)

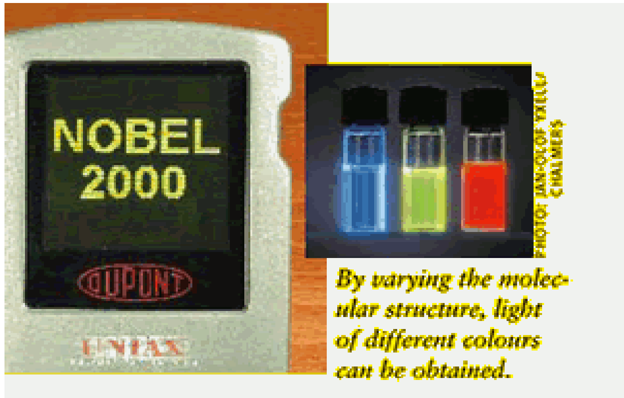
I-V characteristics

Diodes!!!



Why PLEDs?

- Easy and low-cost fabrication
- Solution processability
- Light weight and flexible
- Easy color tuning
  - ✓Spin-coating for mono-color display
  - ✓Ink Jet printing for multi-colors display



http://www.nobel.se/chemistry/laureates/2000/illpres/7.html
http://www.toshiba.co.jp/about/press/2001_05/pr_j3001.htm

Efficiency of Organic EL Devices

$$\eta_{ext} = \eta_{int}\,\eta_p = \gamma\ \eta_r\ \varphi_f\ \eta_p$$

~100% ~25% ~100% ~20%

Maximum external quantum efficiency is ~5%

η_{ext} : external quantum efficiency
η_{int} : internal quantum efficiency
η_p : light out-coupling efficiency
γ : charge carrier balance factor (e/h)
η_r : efficiency of exciton production
φ_f : internal quantum efficiency of luminescence

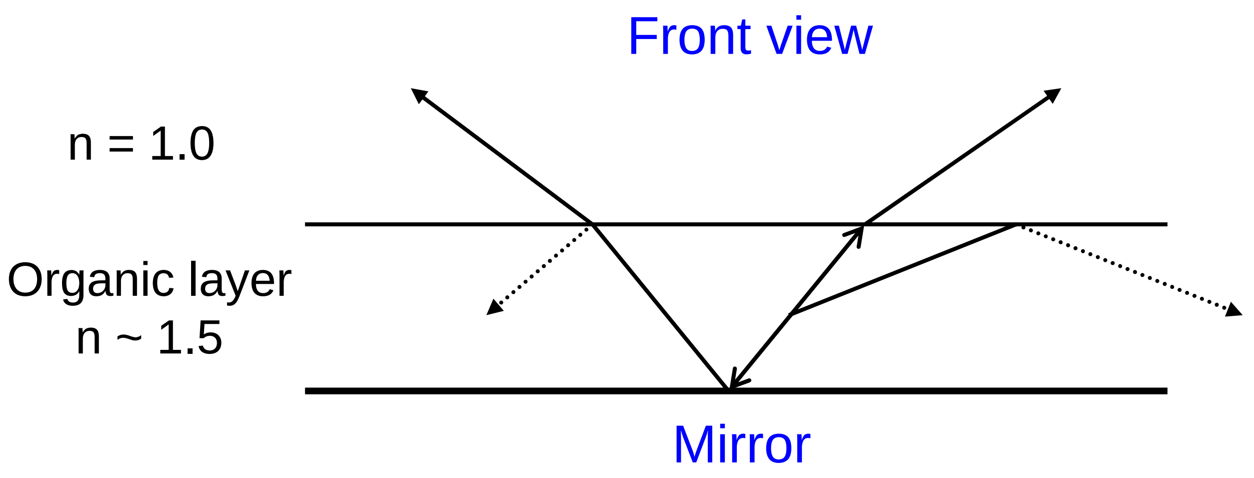
η_p : light out-coupling efficiency

due to total internal reflection loss

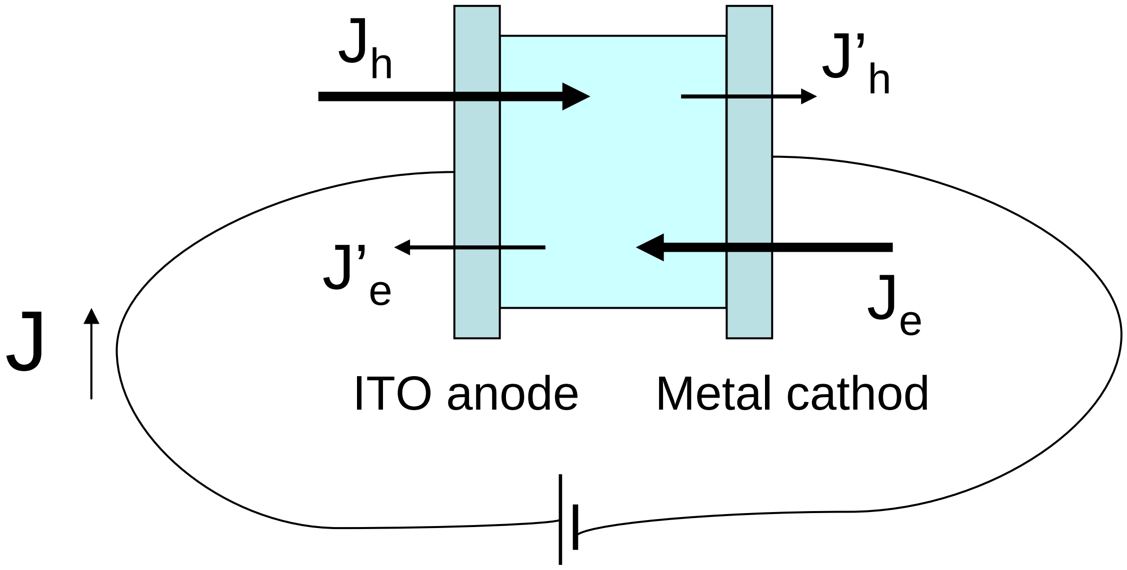
$\eta_p = 1 / (2n^2)$

n : reflection index of the emissive medium

If n ~ 1.5 η_p = 22%



γ : charge carrier balance factor (e/h)



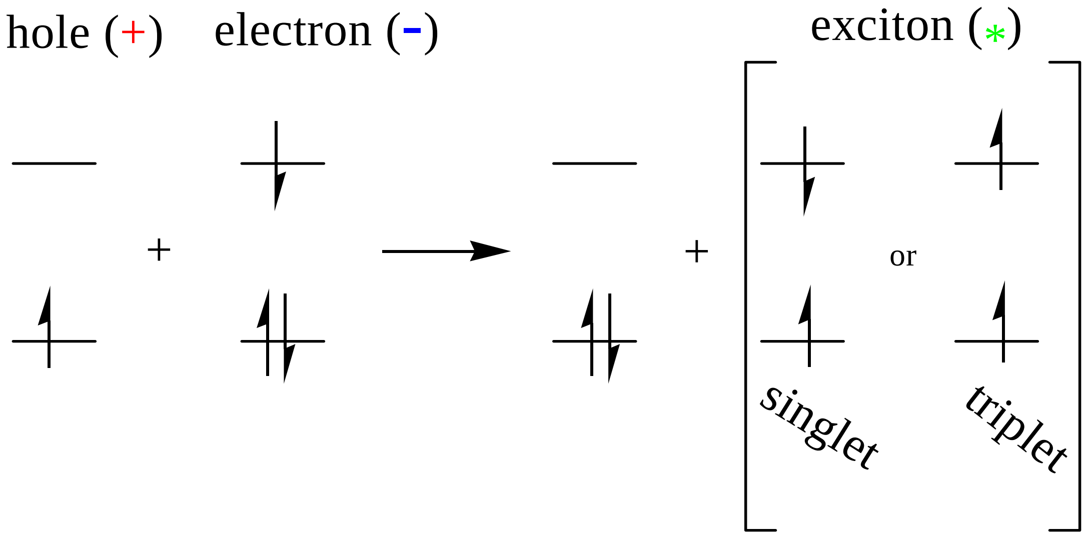
$$\gamma = J_r / J$$

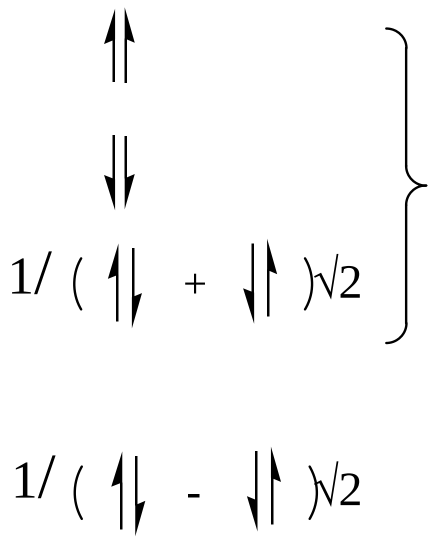
J : circuit current

J_r : current used for charge recombination

$$J = J_h + J'_e = J_e + J'_h$$
$$J_r = J_h - J'_h = J_e - J'_e$$

η_r : efficiency of exciton production

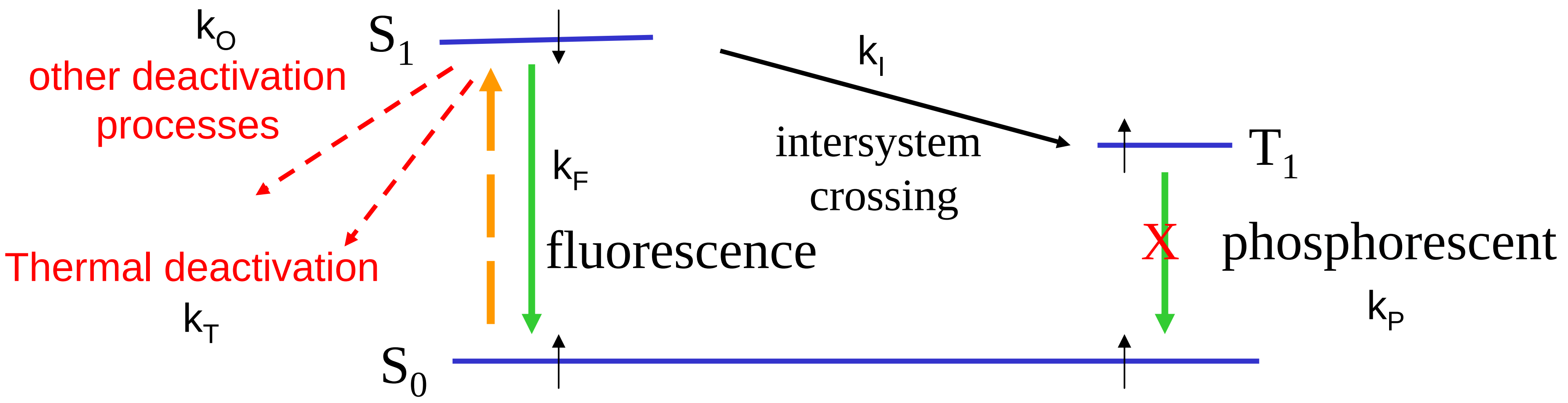




3 symmetric states
Triplets

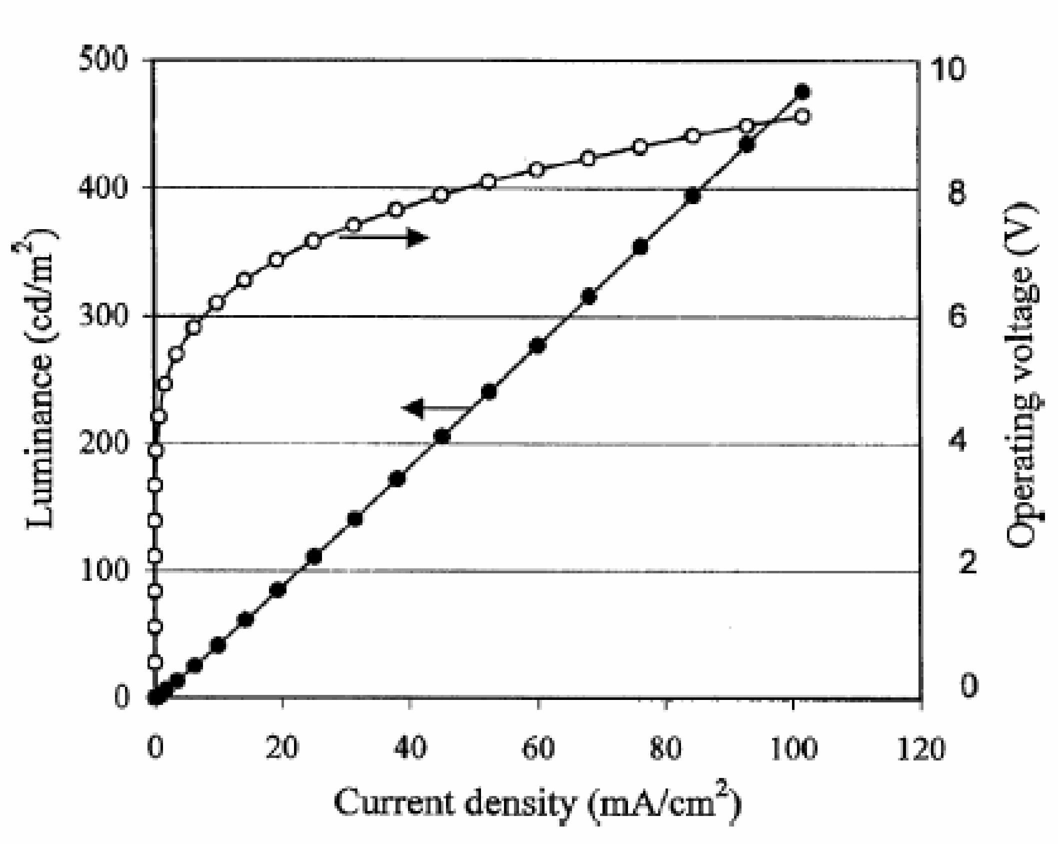
1 antisymmetric state
Singlet

φ_f : internal quantum efficiency of luminescence



$$\varphi_F = \frac{k_F}{k_F + k_I + k_T + k_O}$$

Typical I-L-V curves of an Alq3-based OLED

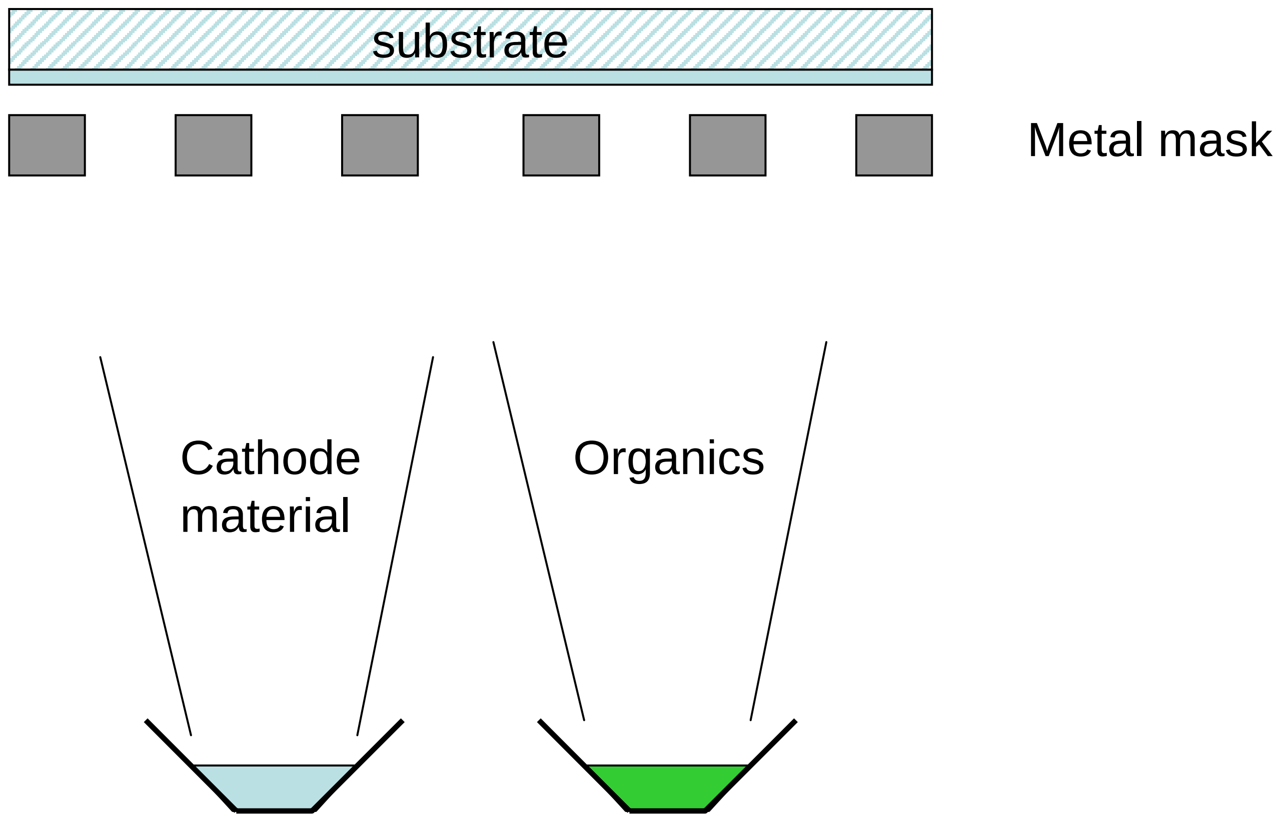


75 nm NPD/75 nm Alq_3

L. S. Hung and C. H. Chen, Mater. Sci. & Eng. R 39, 143 (2002)

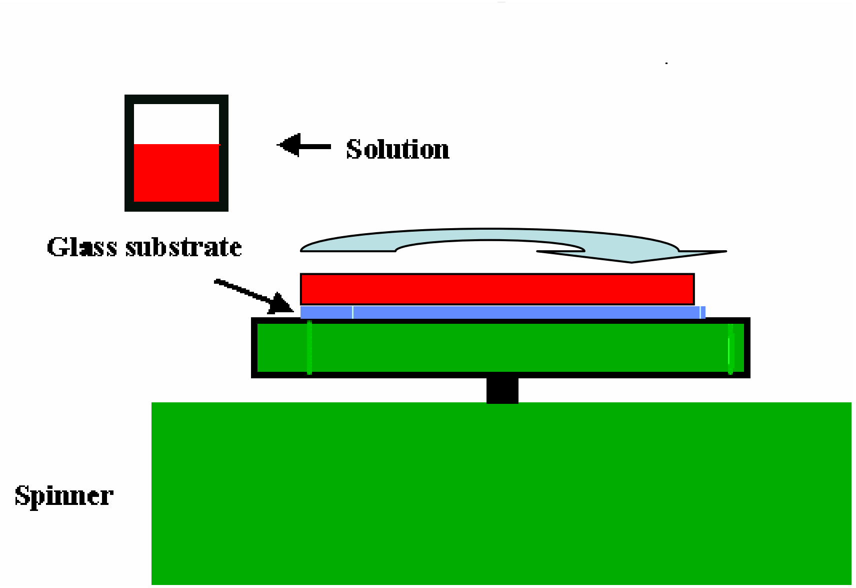
Manufacture of OLEDs

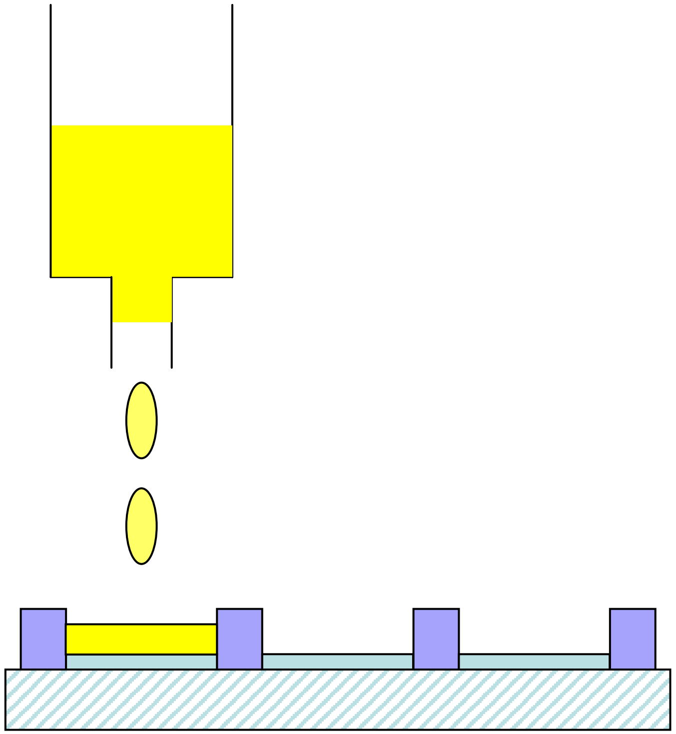
Thermal evaporation



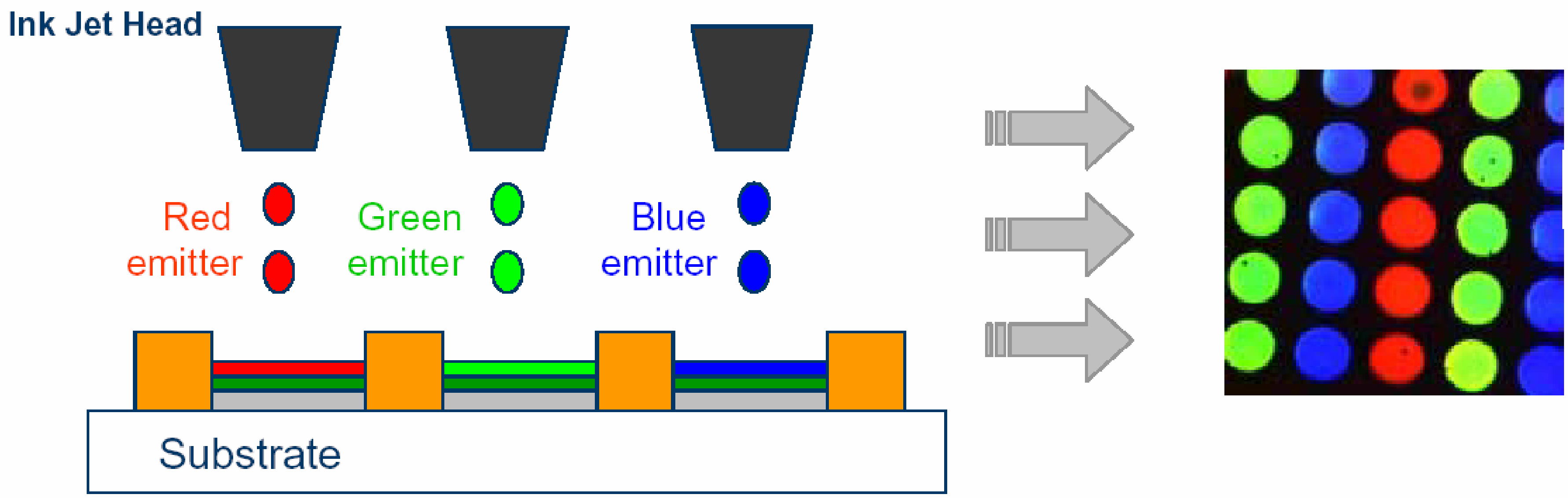
Manufacture of PLEDs

Spin-coating or ink-jet printing





Ink-jet printing to pattern polymers



Ink Jet printing to define and pattern R, G, B emitting subpixels

Efficiency of organic EL Devices

Quantum efficiency: $\eta_{ext} = \eta_{int}\,\eta_p = \gamma\ \eta_r\ \varphi_f\,\eta_p$

η_{ext} : external quantum efficiency
η_{int} : internal quantum efficiency
η_p : light out-coupling efficiency
γ : charge carrier balance factor (e/h)
η_r : efficiency of exciton production
φ_f : internal quantum efficiency luminescence

Power efficiency: $\dfrac{\text{optical power output}}{\text{electrical power input}}$

$$\eta_{pow} = \eta_{ext}\,E_p U^{-1}$$

E_p : the average energy of the emitted photons

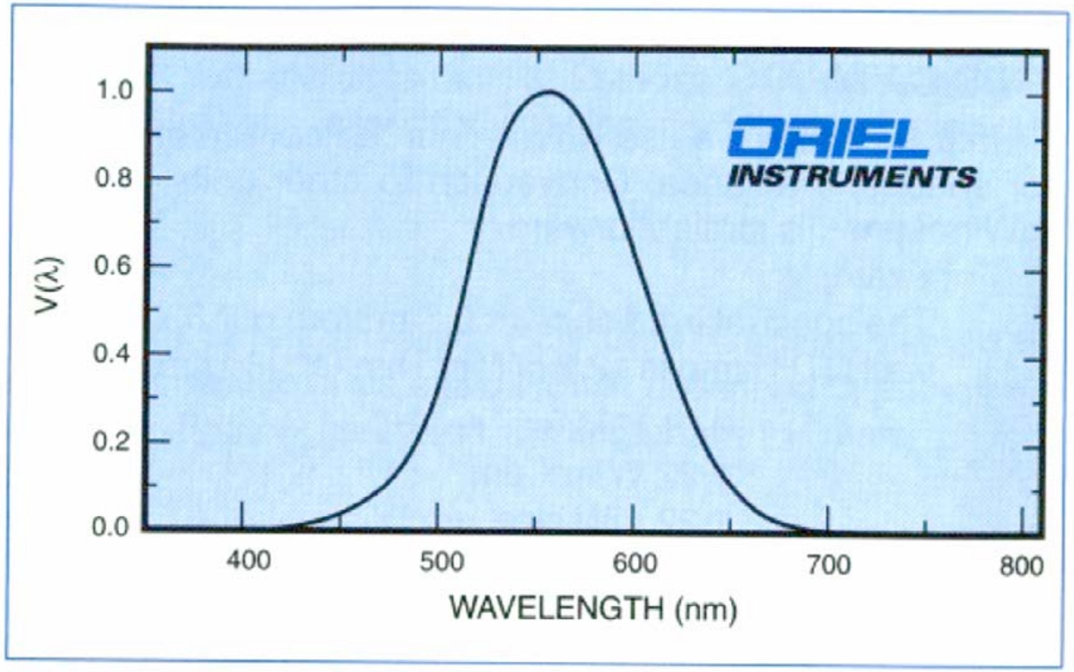
U : the known values of the applied voltage

(lm/W), important for engineer and system design

Efficiency of organic EL Devices

Luminous efficiency: $\eta_{lum} = \eta_{pow} S$

S : the eye sensitivity curves



Current efficiency (Cd/A), important for material evaluation

Efficiency of organic EL Devices – an Example

Device current density : 50 mA/cm^2 at 10V

Brightness : 3500 cd/m^2

Current Efficiency :

$$\frac{3500\ \mathrm{cd/m^2}}{50\ \mathrm{mA/cm^2}} \times \frac{1}{\mathbf{10}} = \boxed{7\ \mathrm{cd/A}}$$

Power Efficiency :

$$\frac{7\ \mathrm{cd/A}}{10\ \mathrm{V}} \times \pi = \boxed{2.2\ \mathrm{lm/W}}$$

Definitions of Efficiencies of OLEDs

Table 1. Definitions of efficiencies used in OLED characterization.

Quantity	Symbol	Units	Expression
OLED Efficiencies:			
External Quantum	η_{ext}	—	$\frac{q\int\lambda I_{det}(\lambda)d\lambda}{hcfI_{OLED}\int R(\lambda)d\lambda}=\frac{\int\lambda I_{det}(\lambda)d\lambda}{fI_{OLED}\int\lambda\eta_{det}(\lambda)d\lambda}$
Internal Quantum	η_{int}	—	η_{ext}/η_c
Wall Plug	$\eta_{W/W}$	—	$P_{OLED}/I_{OLED}V$
Luminous Power	η_P	lm/W	$L_P/I_{OLED}V=\frac{\phi_0\int g(\lambda)I_{det}(\lambda)/R(\lambda)d\lambda}{fI_{OLED}V}$
Luminance	η_L	cd/A	AL/I_{OLED}
Detector Efficiencies:			
Responsivity	R	A/W	$I_{det}/fP_{OLED}=I_{det}/P_{inc}$
External Quantum	η_{det}	—	$hcR/q\lambda$

Definition of terms: λ = wavelength; $I_{det}(\lambda)$ = photocurrent detected for light incident at wavelengths between λ and $\lambda+d\lambda$; $R(\lambda)$ = incremental detector responsivity wavelengths between λ and $\lambda+d\lambda$; $P_{inc}(\lambda)$ = power incident on the detector wavelengths between λ and $\lambda+d\lambda$; q = electronic charge; h = Planck's constant; c = speed of light in vacuum; f = OLED-to-detector coupling factor (<1); P_{OLED} = total optical power emitted by the OLED; I_{OLED} = OLED current; ϕ_o = peak photopic response of the eye; $g(\lambda)$ = photopic response shape function; V = OLED drive voltage to obtain I_{OLED}; L_P = OLED luminous power [lm]; L = OLED luminance [cd/m^2]; A = OLED active area.

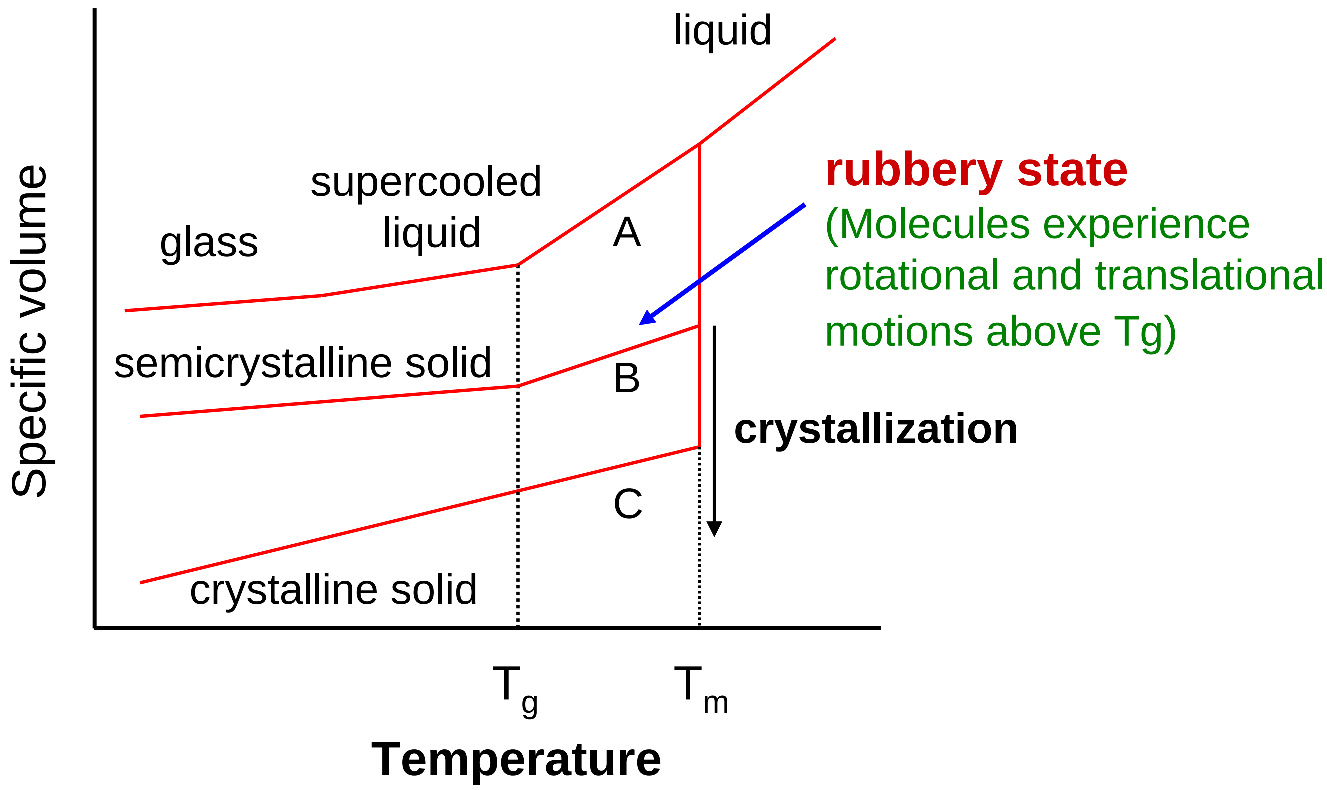
S. R. Forrest *et al*. **Adv. Mat.** 15, 1043 (2003)

Materials for OLEDs

1. High glass transition temperature (T_g)
2. Electrochemically stable
3. Thermally and optically stable
4. High electron or/and hole mobility
5. High photoluminescent
6. Formation of uniform thin films
7. Easy synthesis and purification

Glass transition temperature (Tg)

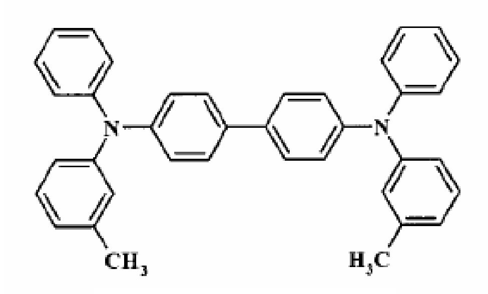
T_g : the Temp. at which the glass transforms from a rigid solid to a supercooled, albeit very viscous, liquid



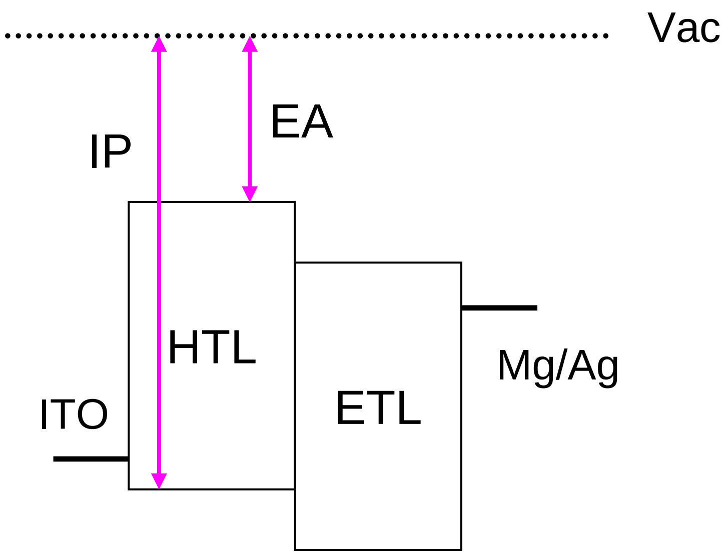
Specific volume: Volume per unit mass

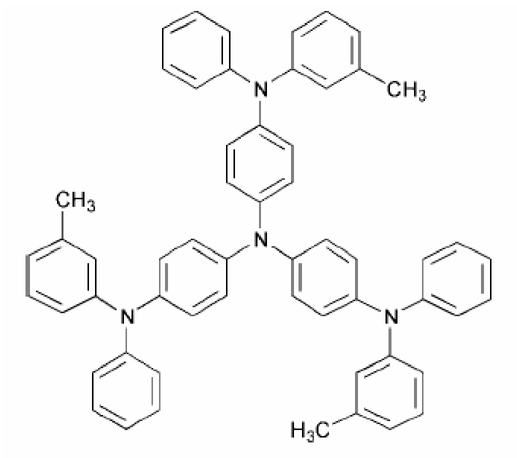
Hole transporting materials

aromatic diamine : good hole injection and transporting capability
electron blocking capability

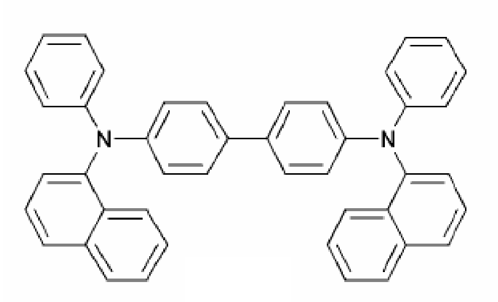


TBD, Tg = 60°C

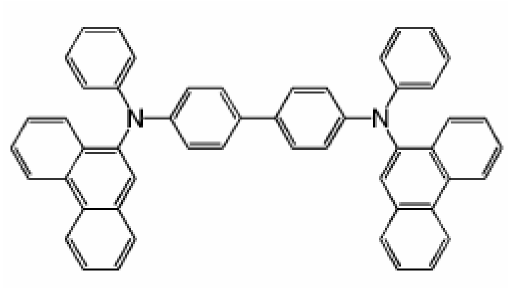




m-MTDATA, Tg = 75°C



α-NPD, Tg = 98°C

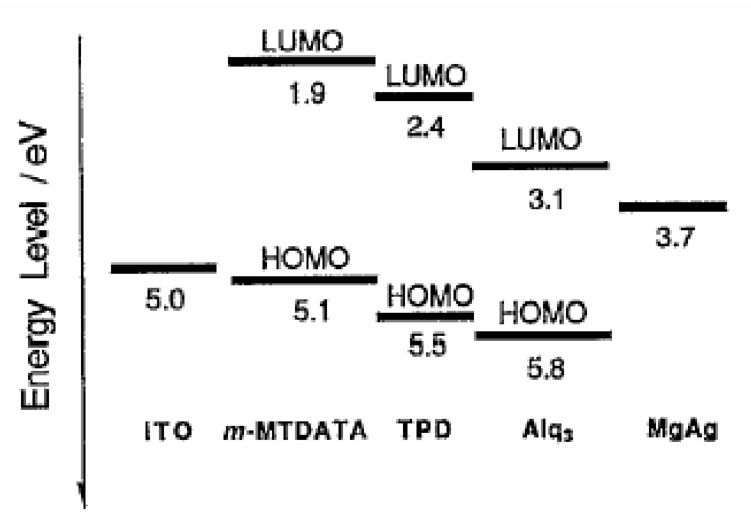


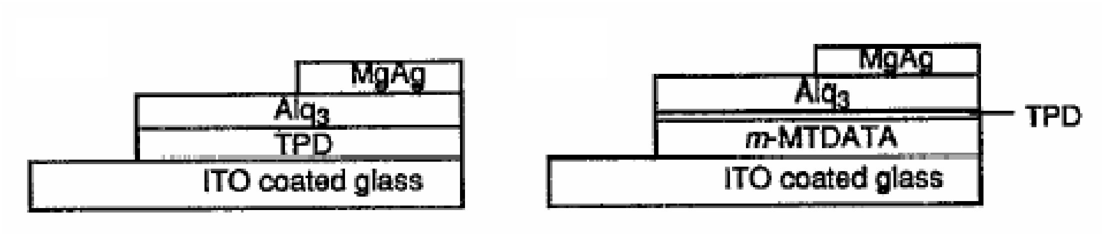
PPD, Tg = 146°C

High T_g can insure stable and pinhole free film

Device performance of double hole HTLs

	m-MTDATA/TPD	TPD
Driving voltage (V)	5.4	6.3
Current density (mA/cm²)	7.1	9.0
Efficiency (lm/W)	2.3	1.6



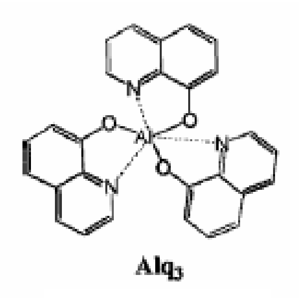


double hole transport layers

Y. Shirota *et al*. APL, 65, 807, (1994)

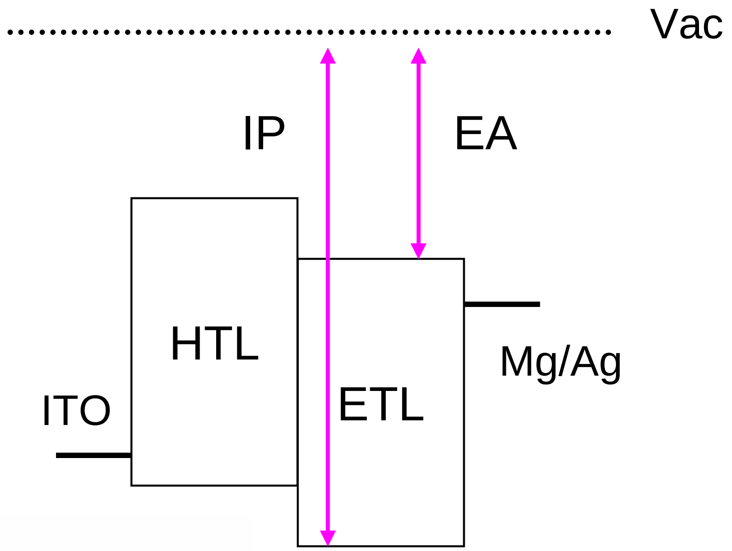
Electron transporting materials

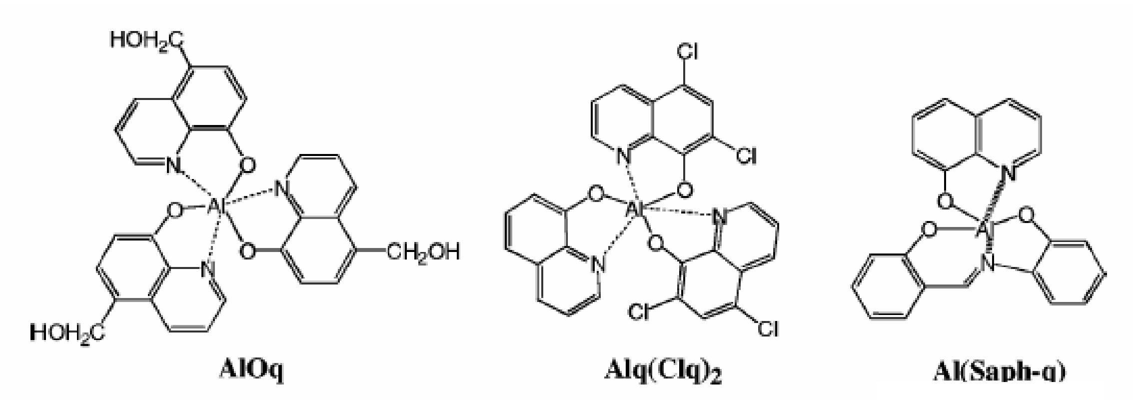
good electron injection and transporting capability
hole blocking capability



Tg = 170°C

thermally and morphologically stable

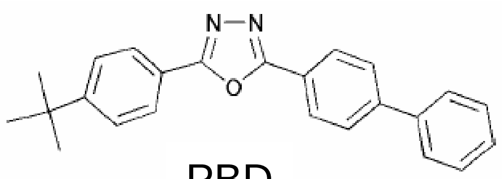




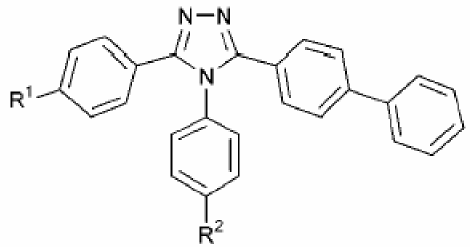
Tg = 226°C

Electron transporting materials

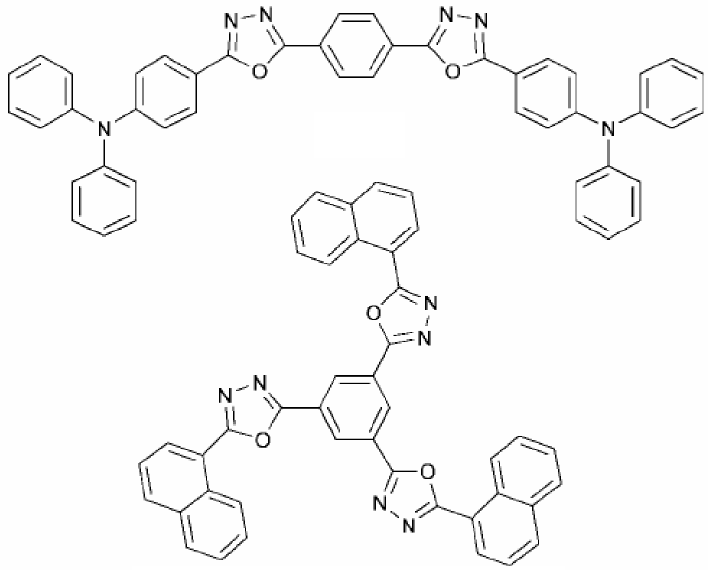
Oxadiazole : ETL and hole blocking layer (large band gap)



PBD



TAZ: R^1 = *t*-Bu; R^2 = H



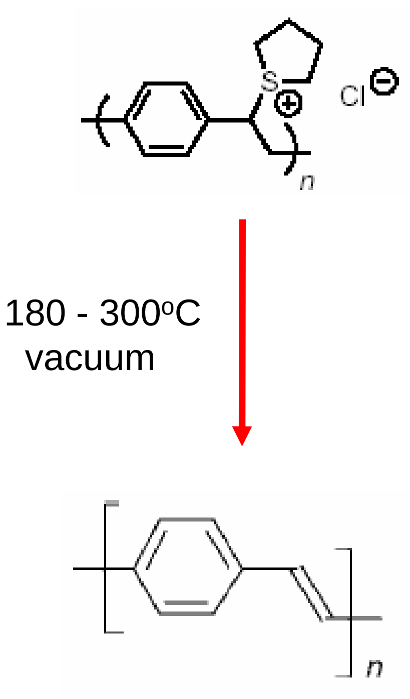
starburst oxadiazole

Disadvantage:
high electron injection barrier

Materials for PLEDs

They are also called
light-emitting polymers (LEPs)

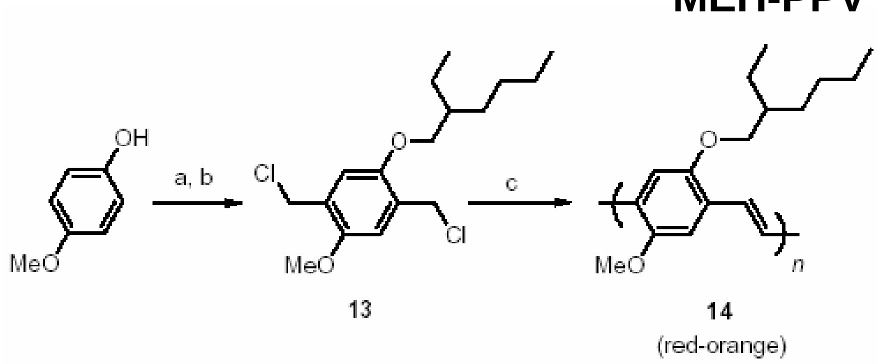
PPV precursor



PPV, first material for PLEDs
green light (λ = 520 & 550 nm)
insoluble
Partially crystalline in the film

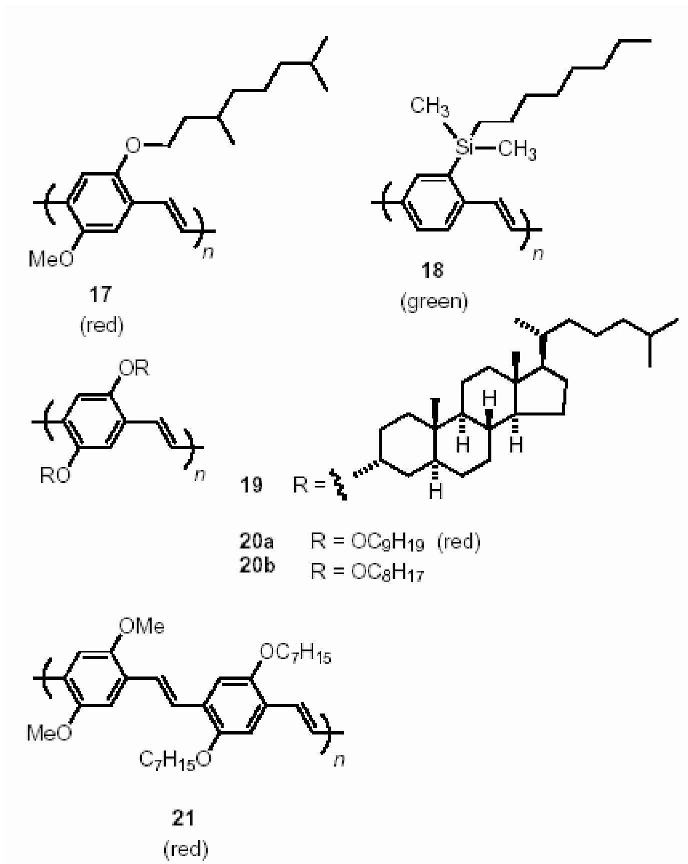
Materials for PLEDs

MEH-PPV

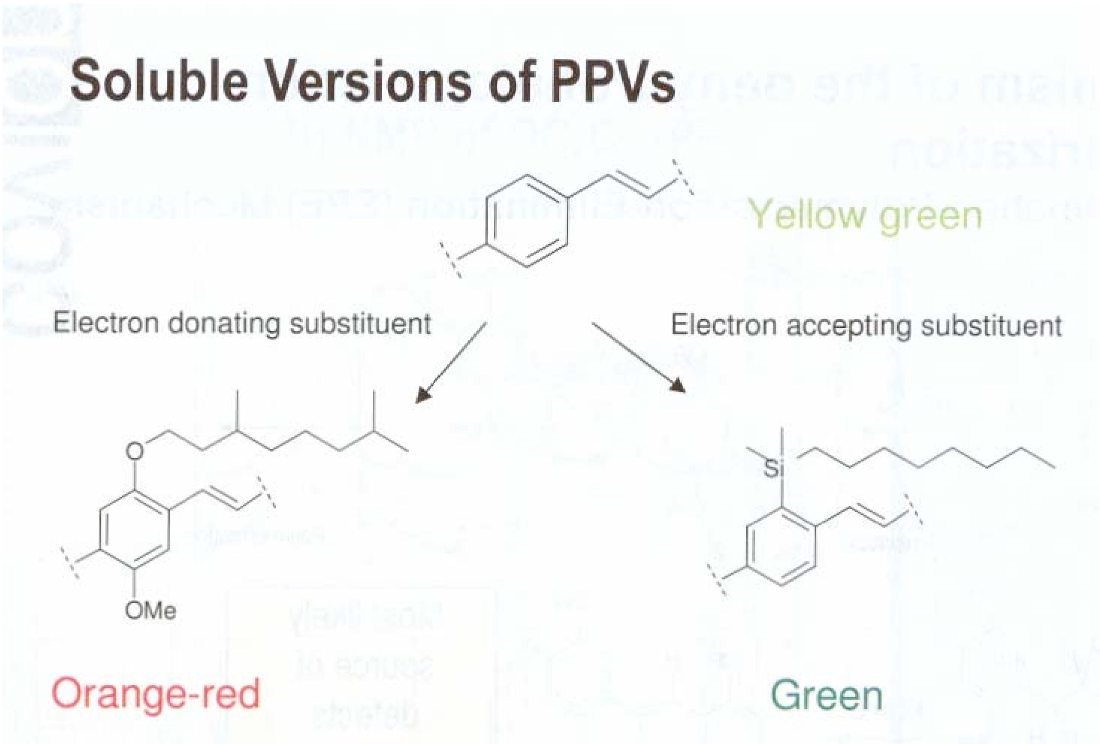


The side chain enhance the solubility in organic solvents

D. Braun and A. J. Heeger, **APL**, 58, 1982, (1991)



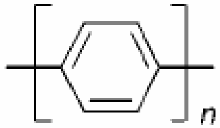
Materials for PLEDs



Tuning of properties (band gap and solubility) can be achieved via substitution

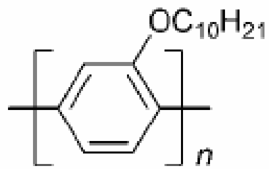
Materials for PLEDs

Blue materials



PPP **9**

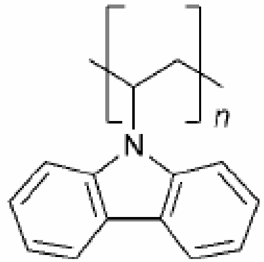
insoluble



10

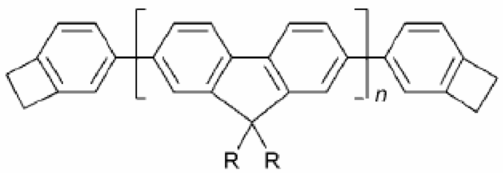
ITO/PVK/10/Ca

~ external 4%



PVK **11**

usually served as hole-transporting/injection material



9,9-dialkyfluorenes

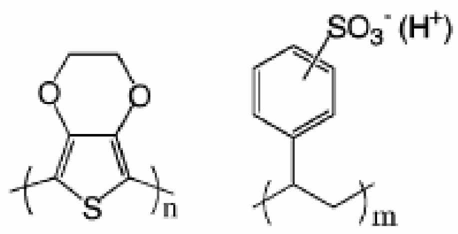
Performance of PPV-based PLEDs with various Emissive colors

LED Configuration	Device Characteristics	Device Lifetime
ITO/MEH-PPV/Ca Single layer device	~2% external QE; 2-3 lm/W; Orange-red color	2,500 h with > 400cd/m^2 initial brightness. tested in inert gas environment
ITO/PPV/Ca Single layer device	~2% external QE ~2 lm/W Yellow-green color	1,000 h with > 100 cd/m^2 initial brightness, encapulated device tested in air
ITO/PVK/DO-PPV/Ca Bilayer device	~4% external QE	Not available

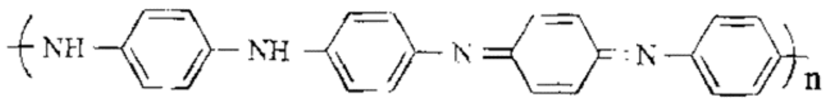
Materials for PLEDs

Hole injection materials (conducting polymer)

Transparent to visible light



PEDT/PSS



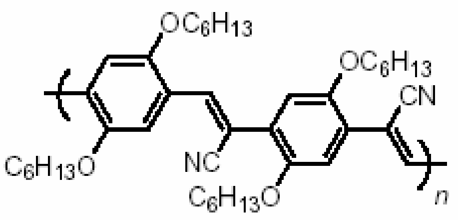
PAni

Y. Yang *et al*. JAP, 77, 694, (1995)

An aqueous gel dispersion
Smooth the ITO surface
(reduce the electrical shorts)
Promote the hole injection

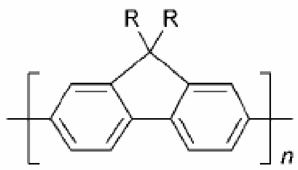
Materials for PLEDs

Electron transporting materials

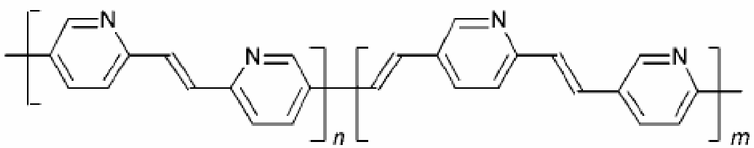


40
(red)

CN-PPV, 590 nm (2.1eV)
ITO/PPV/CN-PPV/cathode



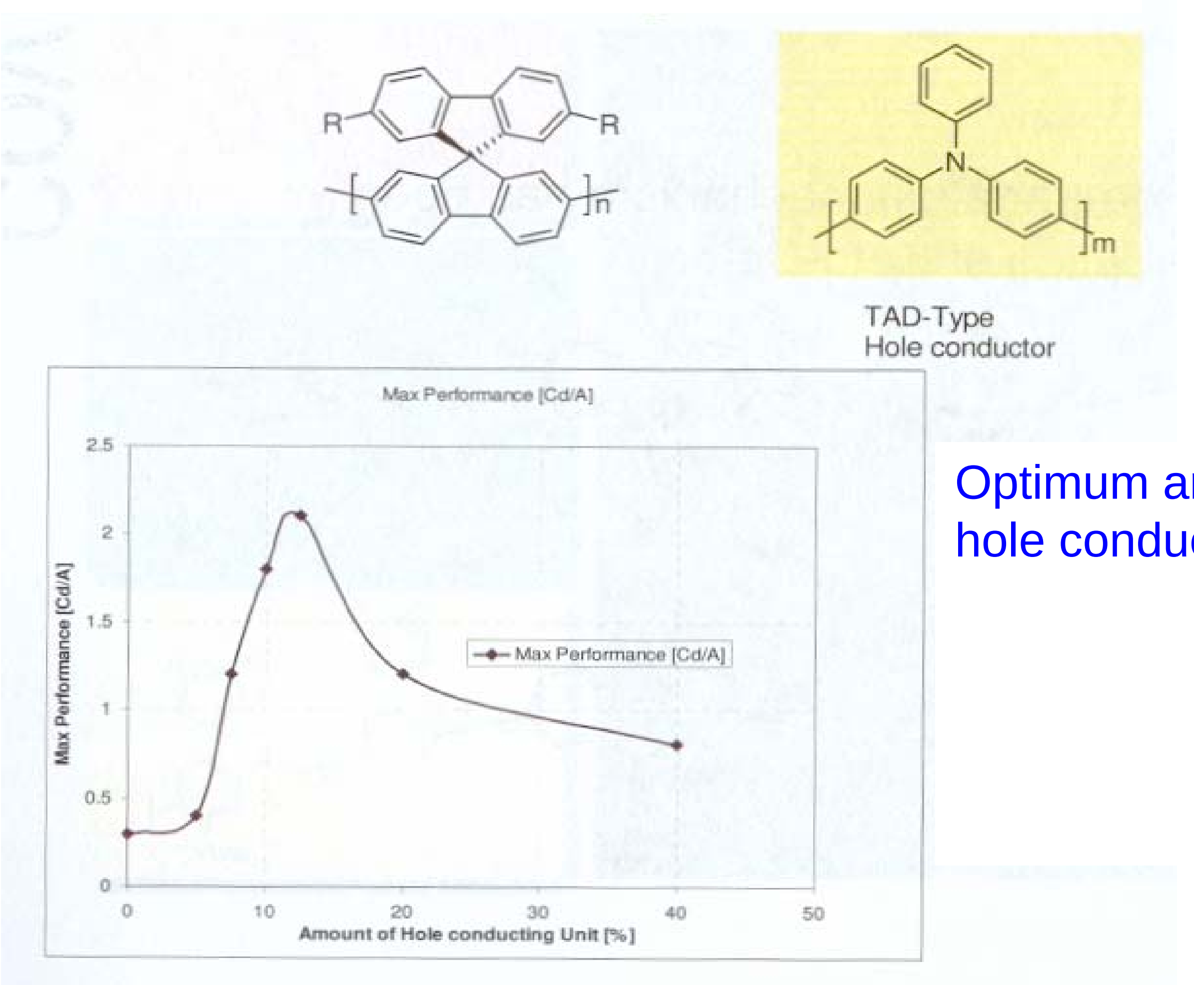
polyfluorene



PPyV **31**

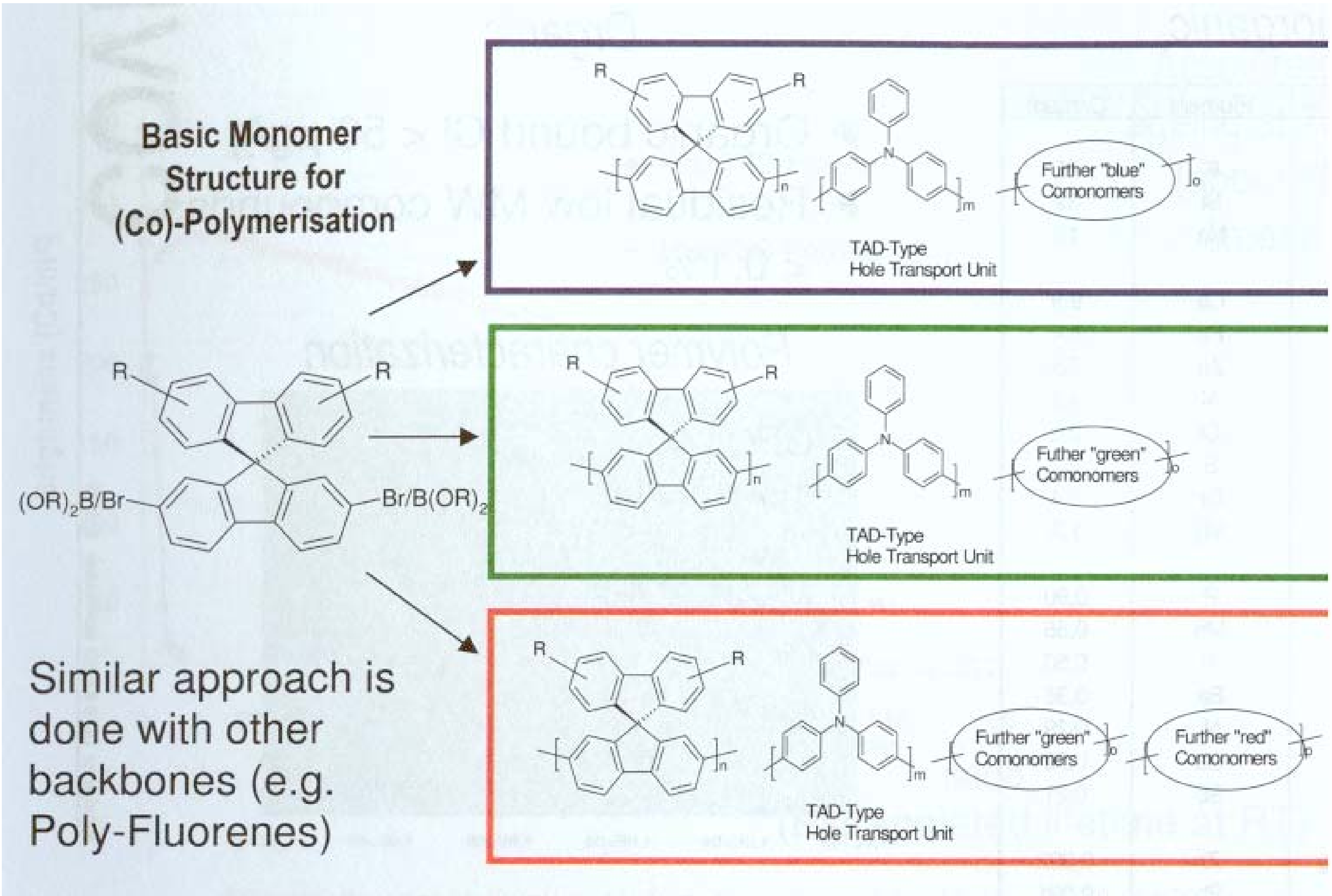
ITO/PPV/PPyV/cathode

Charge Balance



Optimum amount of the hole conducting units

Polymer for RGB



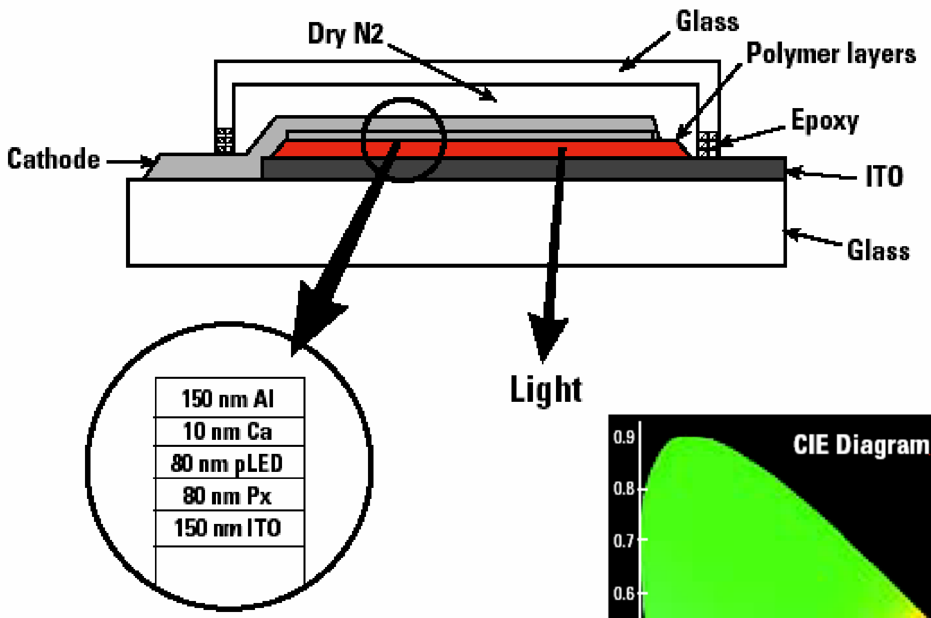
Blue

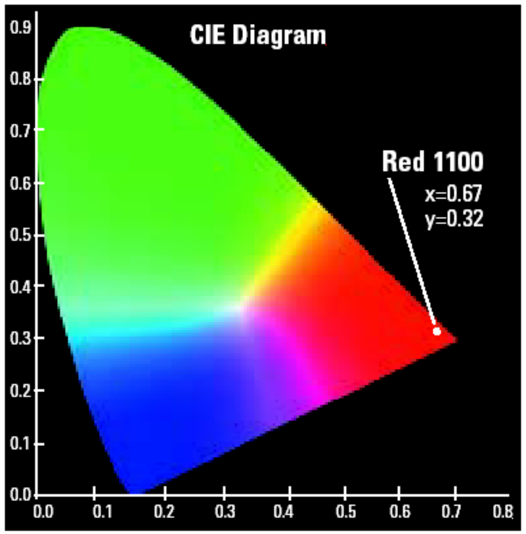
Green

Red

Performance of PF-based PLEDs with various Emissive colors

Schematic Diagram
Dow's Test Device Structure





Typical Device Data[1]

Performance @ 200 cd/m²

Efficiency (cd/A): 1.3
Drive Voltage (V): 3.6
Current Density (mA/cm²): 16.2

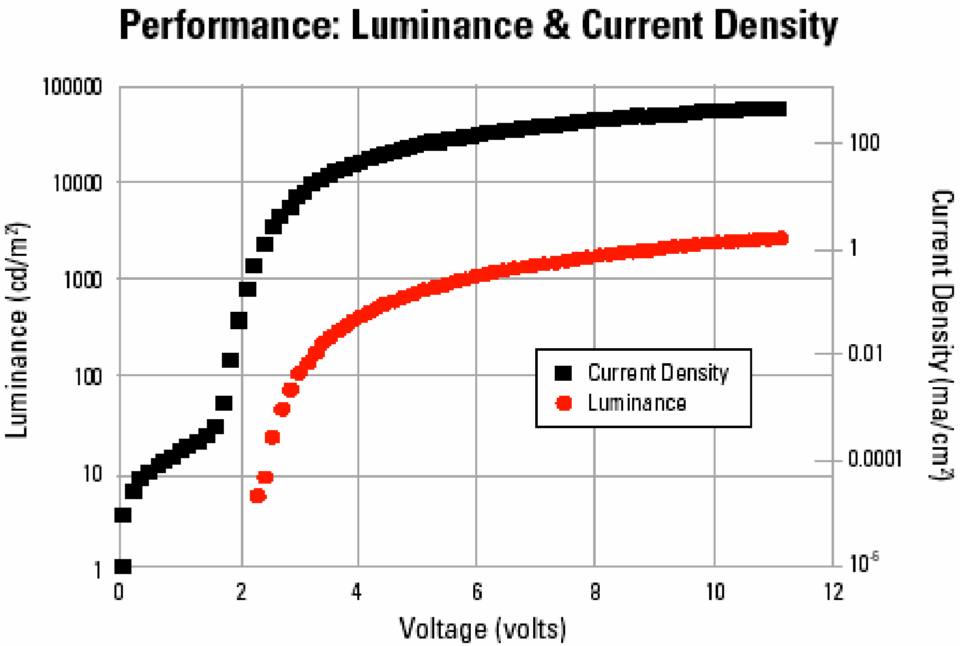
Performance @ 1,000 cd/m²

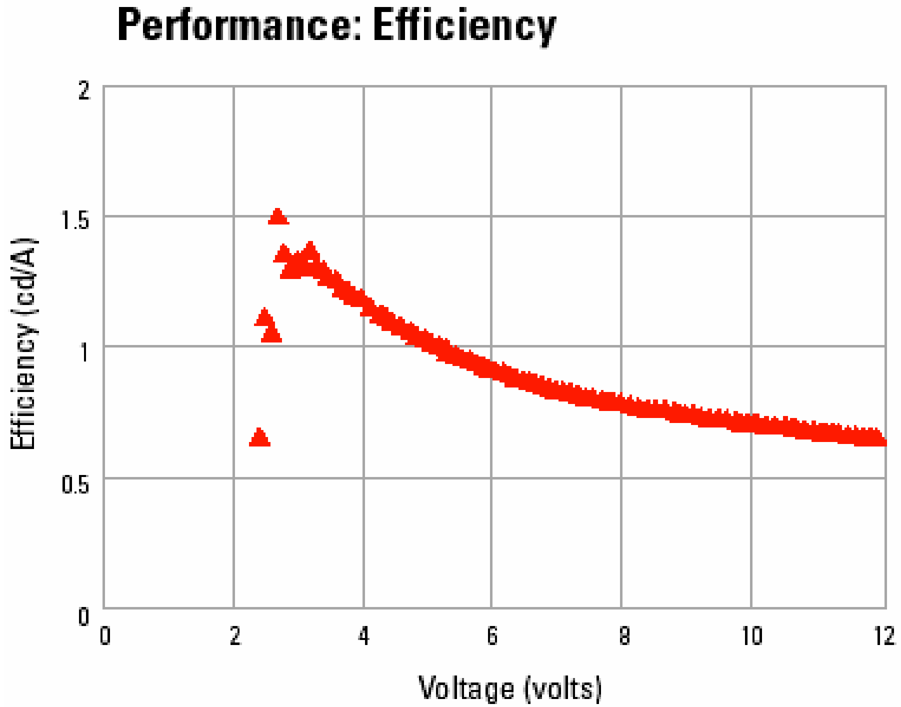
Efficiency (cd/A): 0.9
Drive Voltage (V): 6.2
Current Density (mA/cm²): 110.1

[1] Device architecture may be further optimized to improve performance.

http://www.dow.com/pled/products/index.htm

Performance of PF-based PLEDs with various Emissive colors

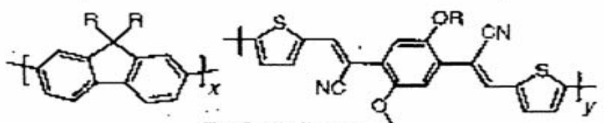
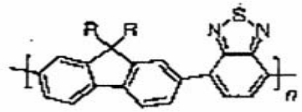




http://www.dow.com/pled/products/index.htm

Examples of Fluorene-based Red and Green LEPs

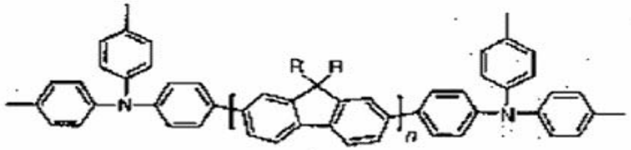
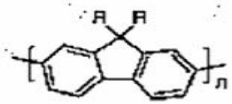
Table I: Representative Examples of Fluorene-Based Red and Green Electroluminescent Polymers.

Emission Color	Red	Green
Structure	 R = 2-ethylhexyl $x:y$ = 81.5%:17.5%	 R = *n*-octyl
Polymer Name	Poly[9,9′-bis(2′-ethylhexyl)fluorene-2,7-diyl-*co*-2,5-bis(2-thienyl-1-cyanovinyl)-1-(2′-ethylhexyloxy)-4-methoxybenzene-5″-5‴-diyl]	Poly[(9,9′-dioctylfluorene-2,7-diyl)-*alt*-benzothiadiazole]
Reference	41	42
UV/PL/EL (λ_{max})	379 nm (film)/620 nm (film)/630 nm	.../545 nm (film)/545 nm (film)
Efficiency	ϕ_{PL} 34% (solution)	ϕ_{EL} 3.86% (external) at 5000 cd/m^2
Light Switch-On (V)	5 V	7 V
Device Structure	ITO/PEDOT:PSS/*polymer*/LiF/Ca	ITO/*polymer*/Al
Polymer Characteristics	M_n 22 K, MWD 2.7 (PS standards) statistical copolymer	Alternating fluorene-thiadiazole copolymer

Notes: PL is photoluminescence; EL is electroluminescence; ϕ is quantum yield; ITO is indium tin oxide; PEDOT:PSS is poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate).

Examples of Fluorene-based Blue LEPs

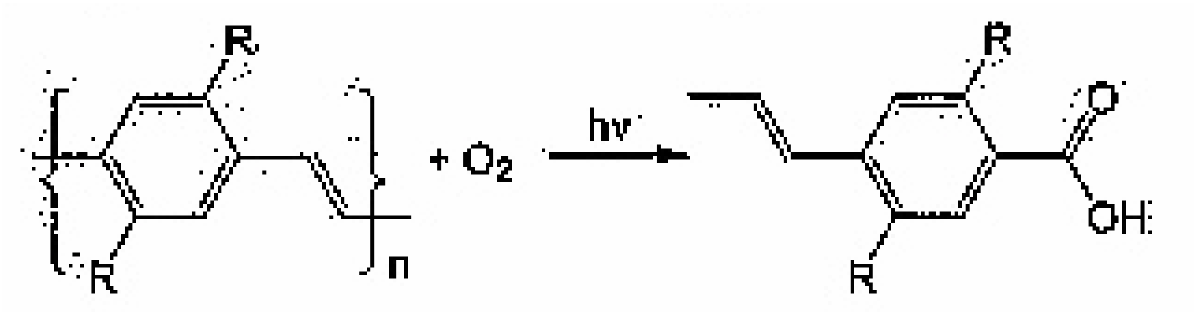
Table II: Representative Examples of Fluorene-Based Blue Electroluminescent Polymers.

Emission Color	Blue	Blue
Structure	 R = 2-ethylhexyl	 R = *n*-octyl
Polymer Name	Poly[9,9′-bis(2-ethylhexyl)fluorene-2,7-diyl] end-capped with *N,N′*-bis(4-methylphenyl)-*N*-phenylamine	Poly(9,9′-dioctylfluorene-2,7-diyl) (PF8, PFO)
Reference	43	44
UV/PL/EL (λ_{max})	.../.../420 nm, 440 nm	380 nm (film)/420 nm (film)/ 440 nm
Efficiency	1.1 cd/A at 8.5 V	ϕ_{EL} 1.3 % (external) at 200 cd/m^2
Light Switch-On (V)	3.5 V	2.7 V
Device Structure	ITO/PEDOT:PSS/*polymer*/Ca	ITO/PEDOT:PSS/*polymer*/Ca
Polymer Characteristics	M_n 48 K, MWD 1.6 (PS standards) linear homopolymer (end-capper feed ratio: 4 mol%)	M_n 43 K, MWD 1.4 (PS standards) linear homopolymer

Notes: PL is photoluminescence; EL is electroluminescence; ϕ is quantum yield; ITO is indium tin oxide; PEDOT:PSS is poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate).

Polymer degradation

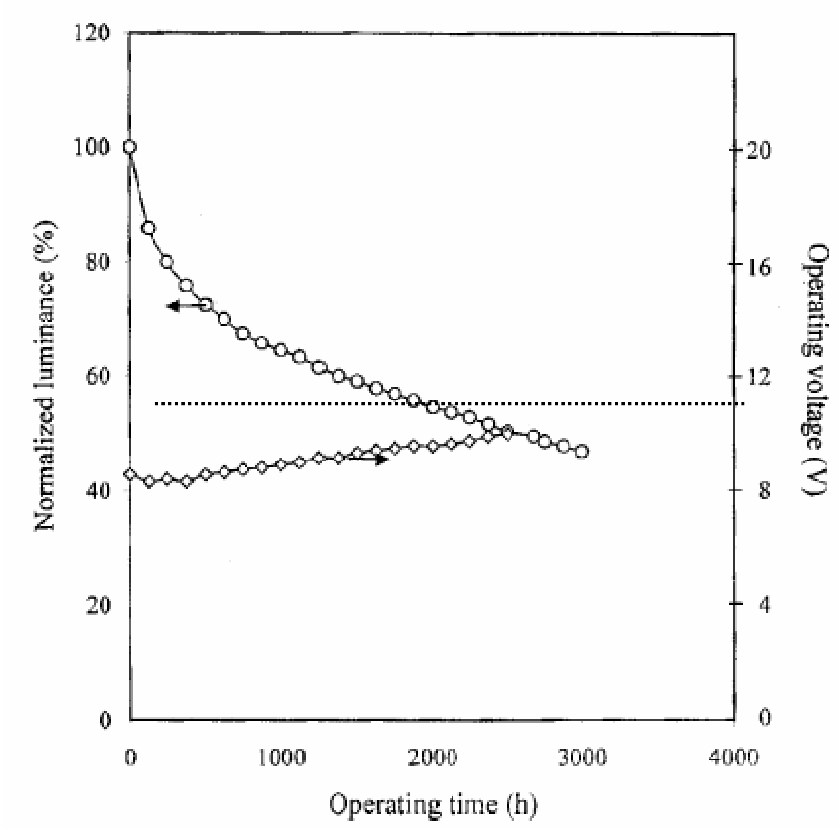
Photo-oxidation of polymer



Loss of double bond (conjugation)

Reliable issues for OLEDs

Anode contacts
Excited state reactions
Crystallization
Thermal stability
Self-heating in operation
Impurities
High local field
Reaction of cathodes with moisture



Summary

Small Molecular LEDs

Blue	QE= ~5%	5~8 lm/W	over 10,000 hrs (@1000cd/m^2)
Green	QE= ~5%	10~15 lm/W	over 10,000 hrs
Red	QE= ~2-3%	1~3 lm/W	over 10,000 hrs

Polymer LEDs

Blue	QE= ~5%	2.5 lm/W	5,000 hrs (@1000cd/m^2)
Green	QE= ~5%	15 lm/W	over 10,000 hrs
Red	QE= ~2-3%	1~3 lm/W	over 10,000 hrs

2004 SID seminar notes -- Prof. Kido