Light Emitting Diodes for Full Color Display and Solid State Lighting

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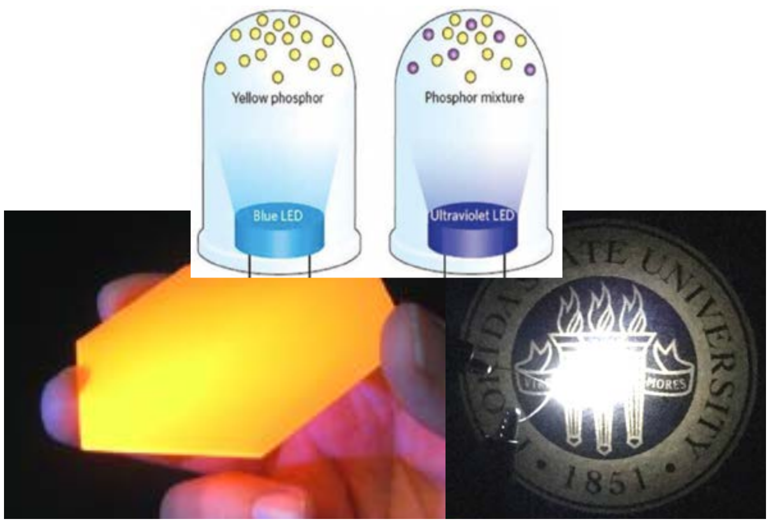
Light Emitting Diodes

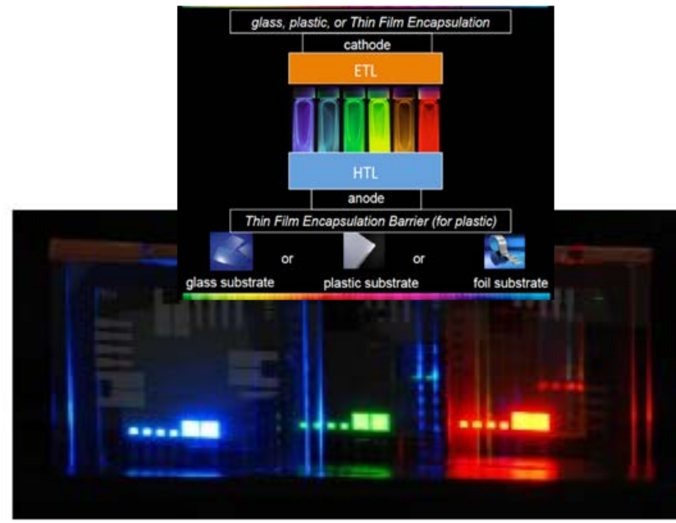
Photoluminescence (PL Mode)

- Activated by light energy
- Conversion color from other light sources
- Light with shorter wavelength (higher energy)

Electroluminescence (EL Mode)

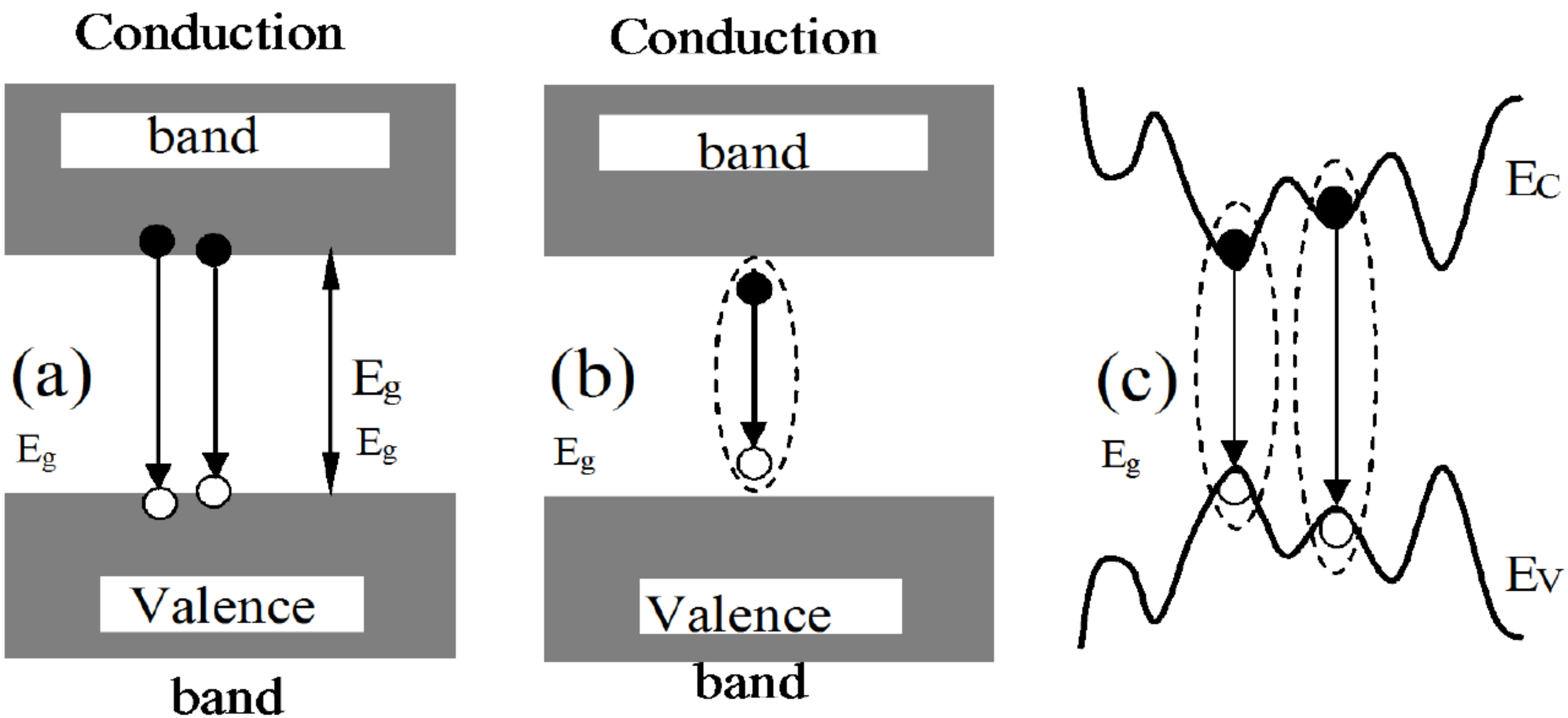
- Activated by electronic energy
- Direct emission of colored light
- OLEDs, QLEDs, PeLEDs, etc.





Generation of Light in Semiconductor LEDs

Recombination of electrons and holes



Intrinsic radiative transitions in semiconductors:

(a) Band-to-band transitions

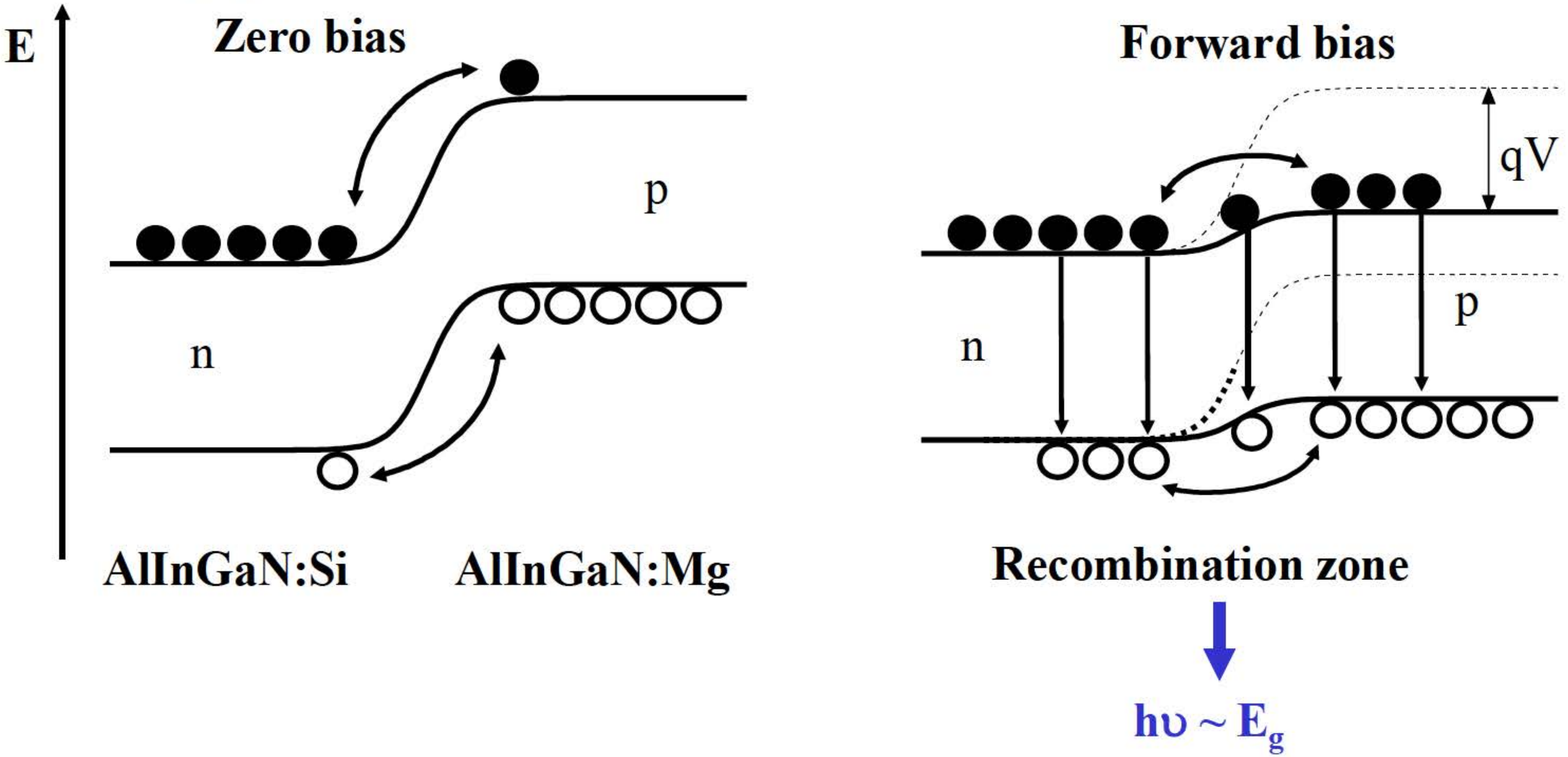
(b) Free-exciton annihilation

(c) Recombination of localized excitons by potential fluctuations in the bands

Generation of Light in Semiconductor LEDs

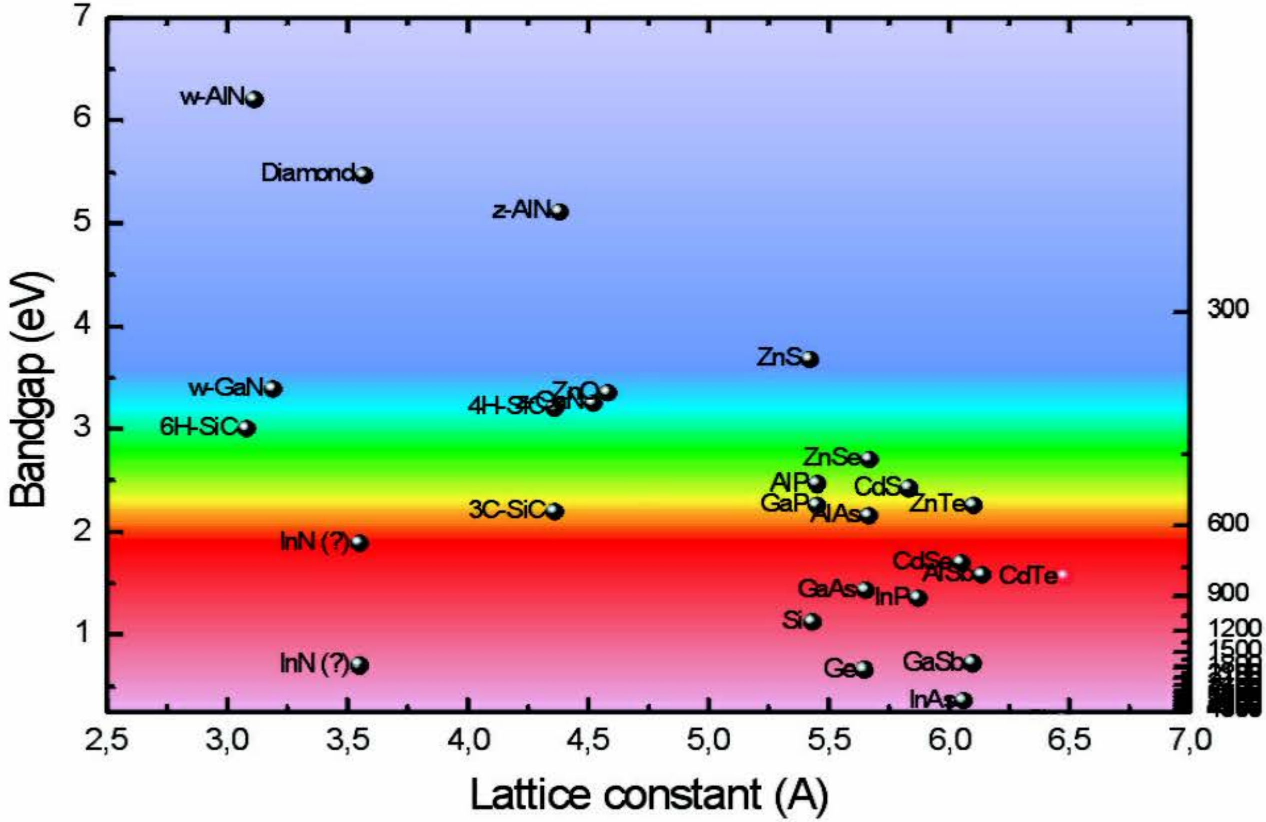
Principle of semiconductor LED

Recombination of electrons and holes at the p/n junction according to the energy and momentum conservation rule ⇒ Energy of the emitted photon corresponds to the band gap



Generation of Light in Semiconductor LEDs

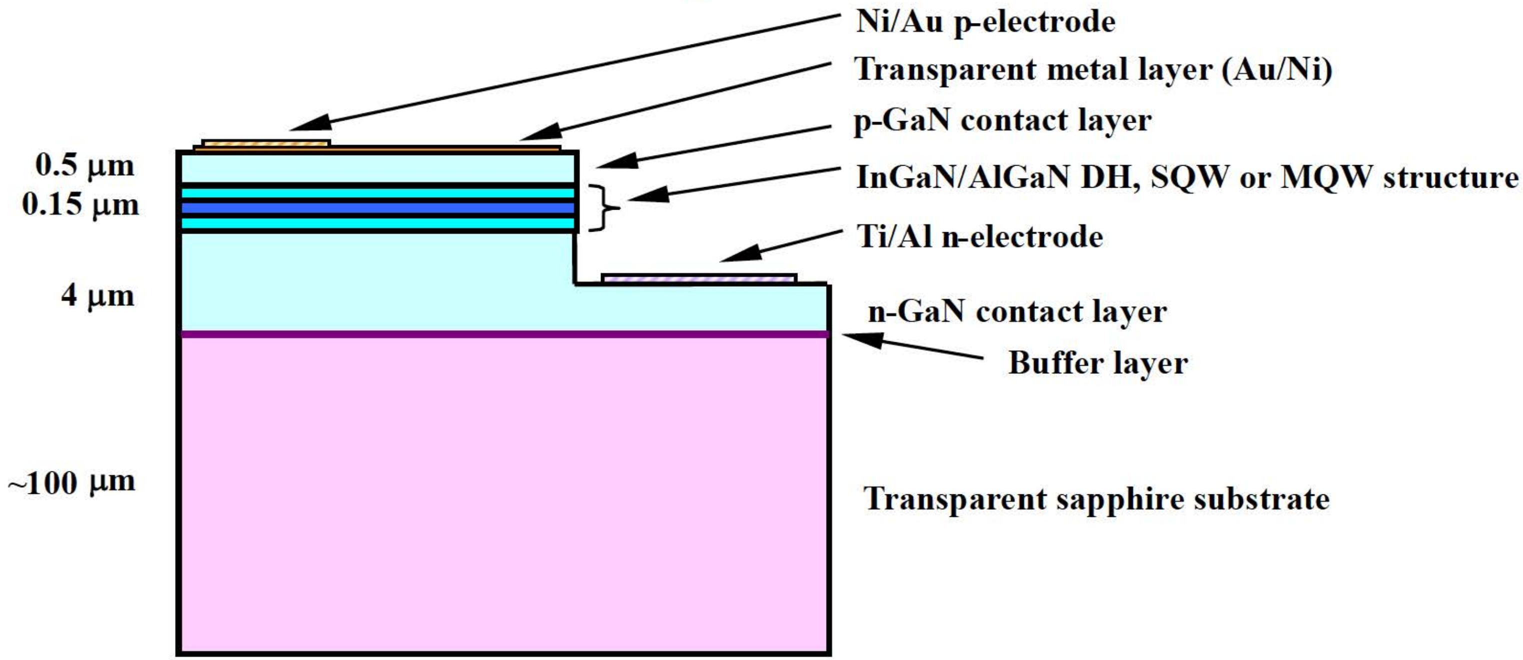
Band gap of suitable semiconductor materials

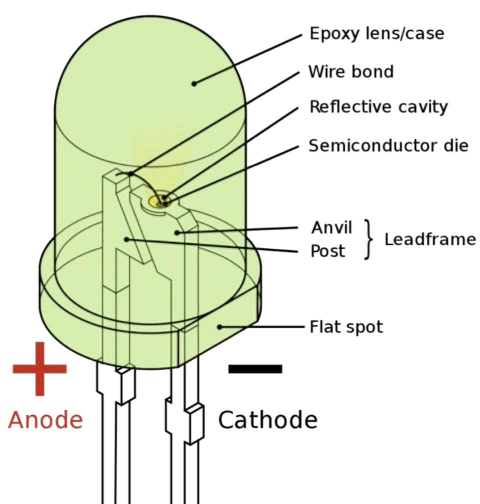


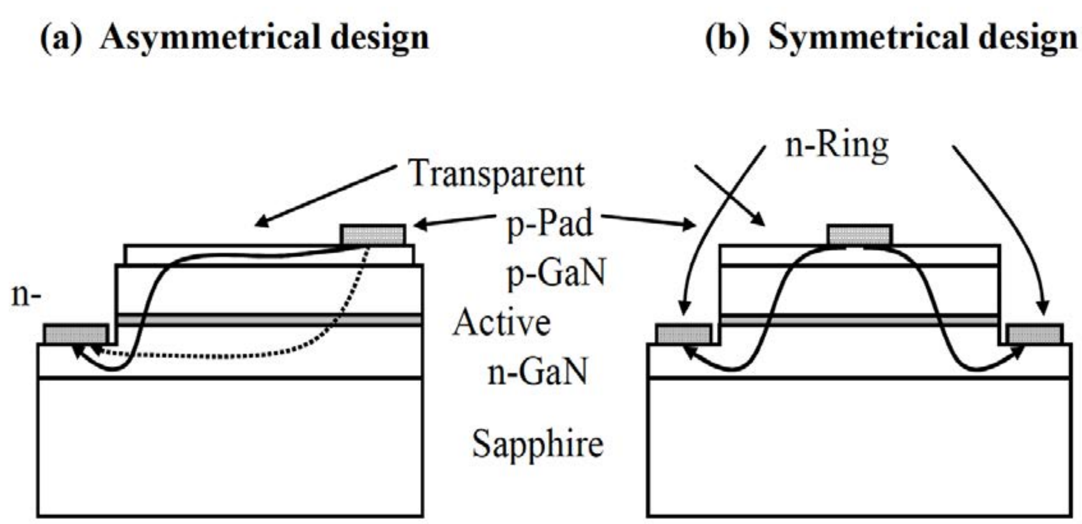
AlN	6.2 eV	(200 nm)	AlP	2.5 eV (500 nm)
GaN	3.5 eV	(370 nm)	GaP	2.3 eV (520 nm)
InN	0.9 eV	(1400 nm)	InP	1.4 eV (900 nm)

Chip Structure of LEDs

Structure of a semiconductor LED chip

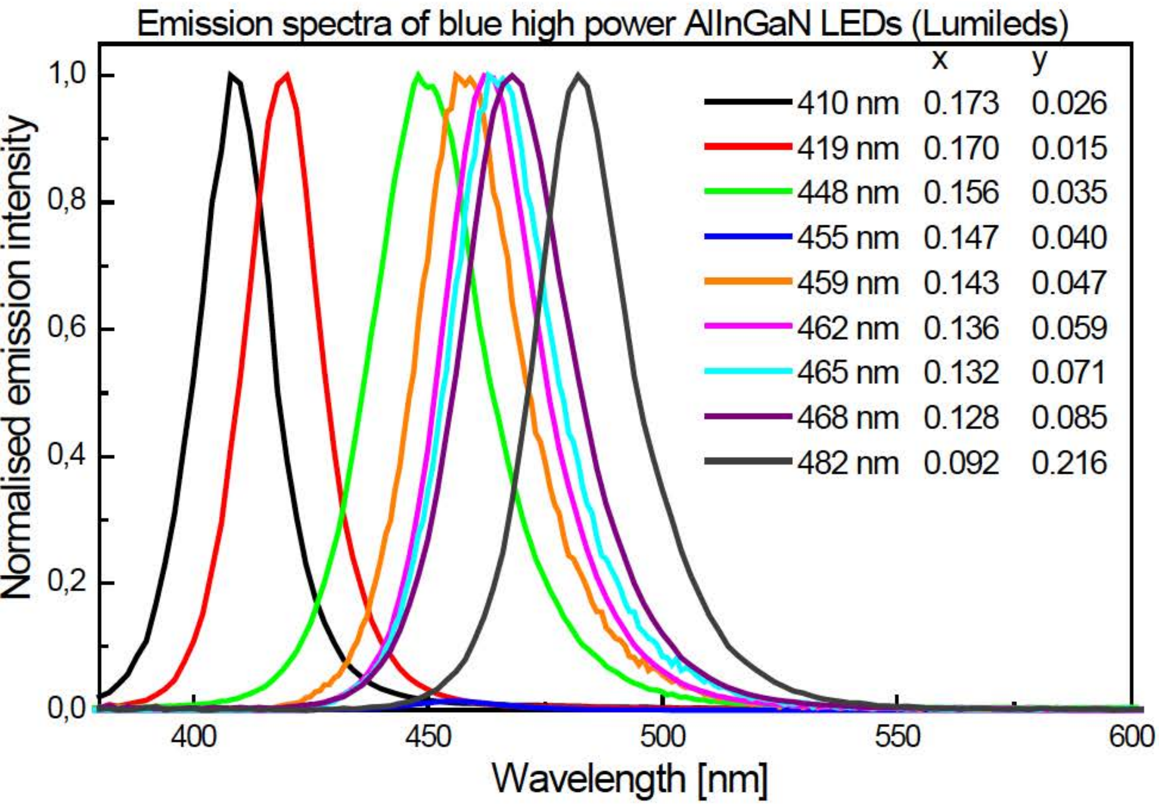






Spectra of LEDs

(Al,In,Ga)N LEDs



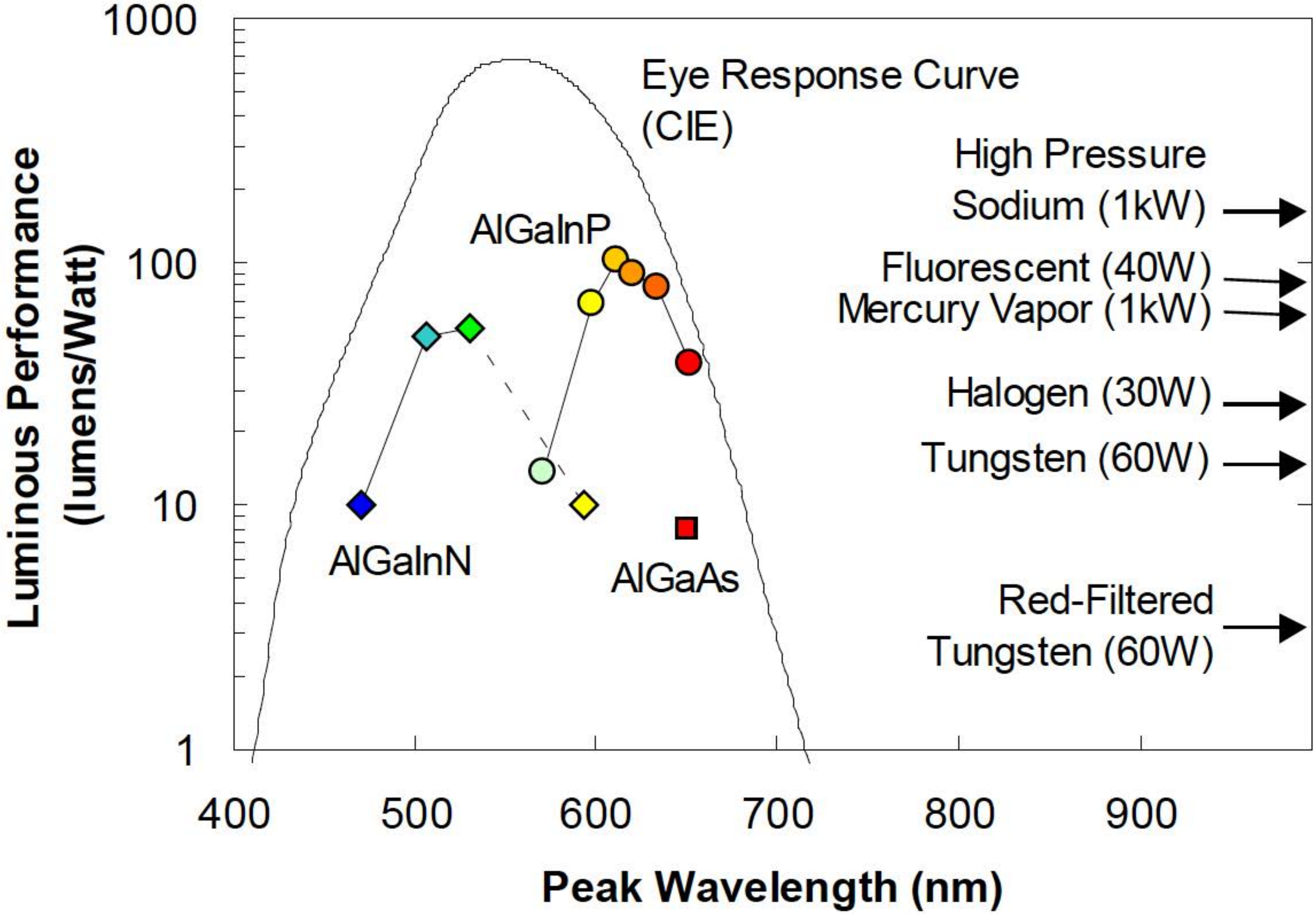
(Al,In,Ga)N forms a complete solid solution series

<u>Increasing In-concentration</u>

- **Energy of the (In,Ga)N quantum well transition decreases**
- **Emission bands broaden**
- **Decrease in quantum yield due to defects**

Evolution of LED Light Sources

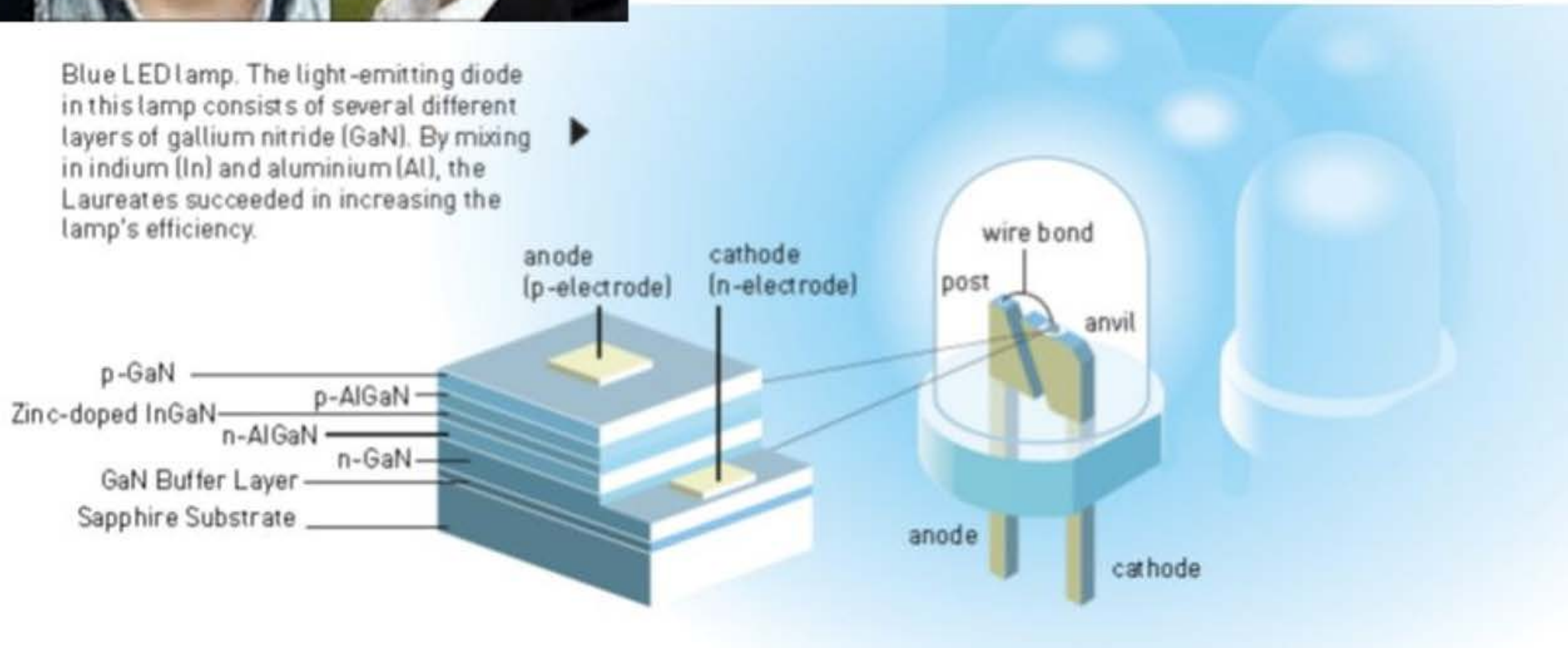
Luminous efficiency of (Al,In,Ga)N, (Al,In,Ga)P and (Al,Ga)As LEDs (Stand 2002, source: Lumileds)



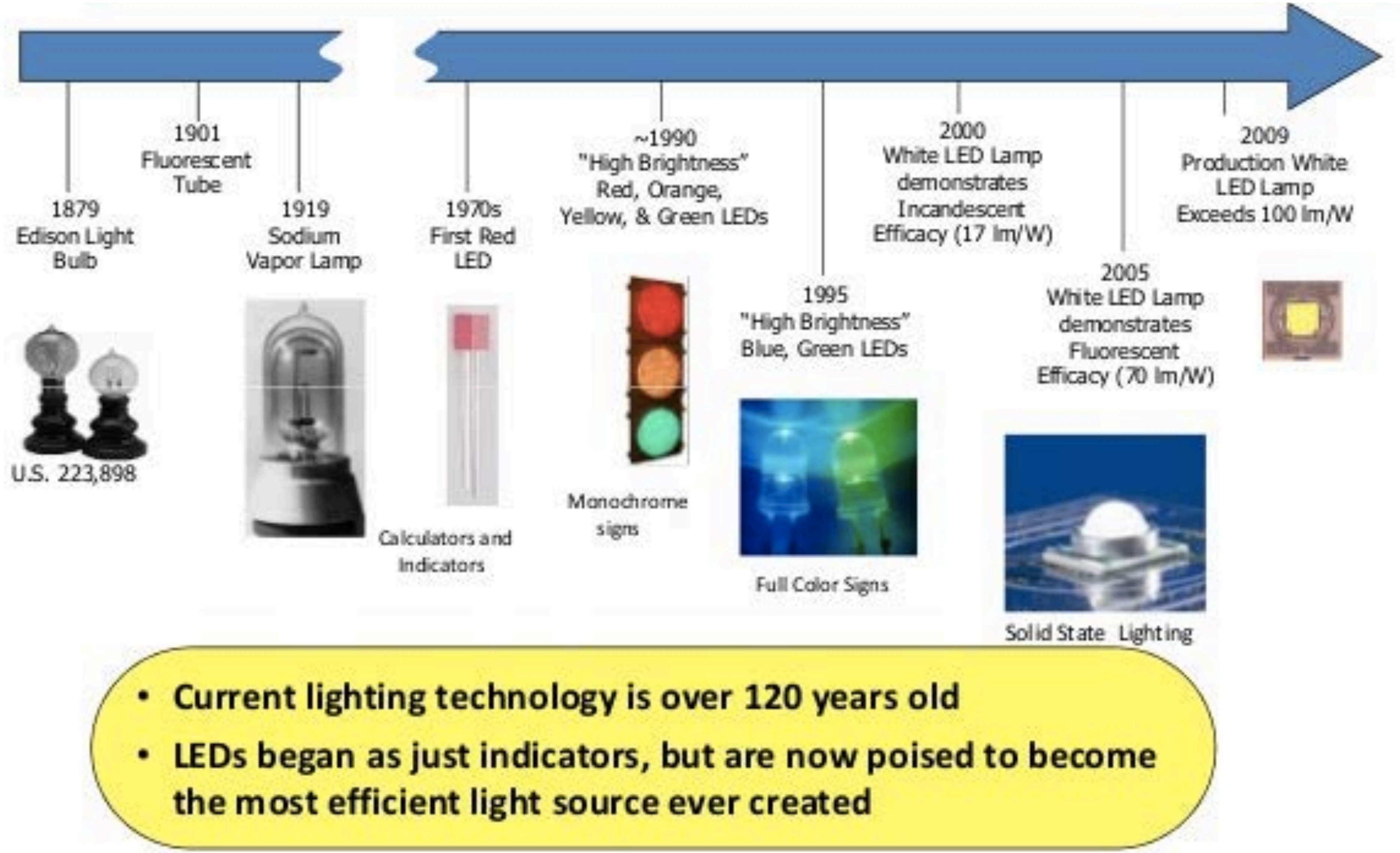
2014 Nobel Prize in Physics

Isamu Akasaki, Hiroshi Amano *and* ***Shuji Nakamura***

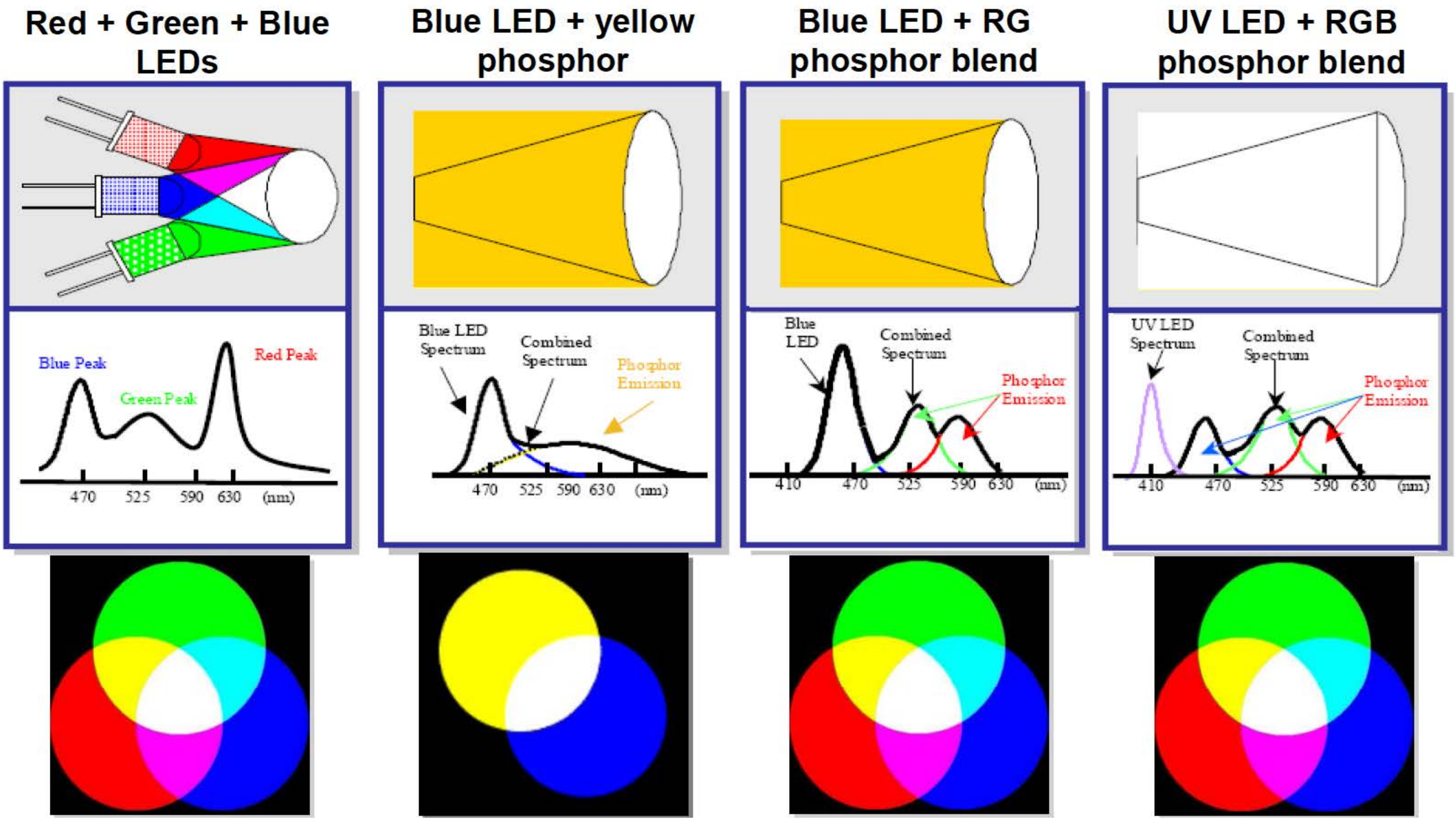
"…are rewarded for inventing a new energy - efficient and environment-friendly light source – the blue light-emitting diode (LED). "



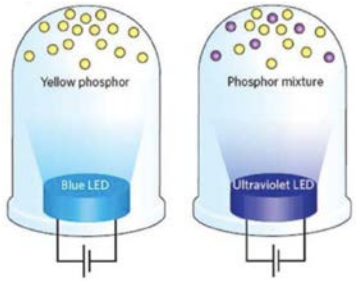
Evolution of LED Light Sources

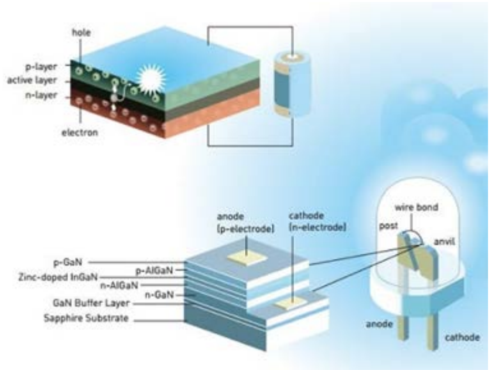


Concepts of White LEDs



Optically Pumped WLEDs



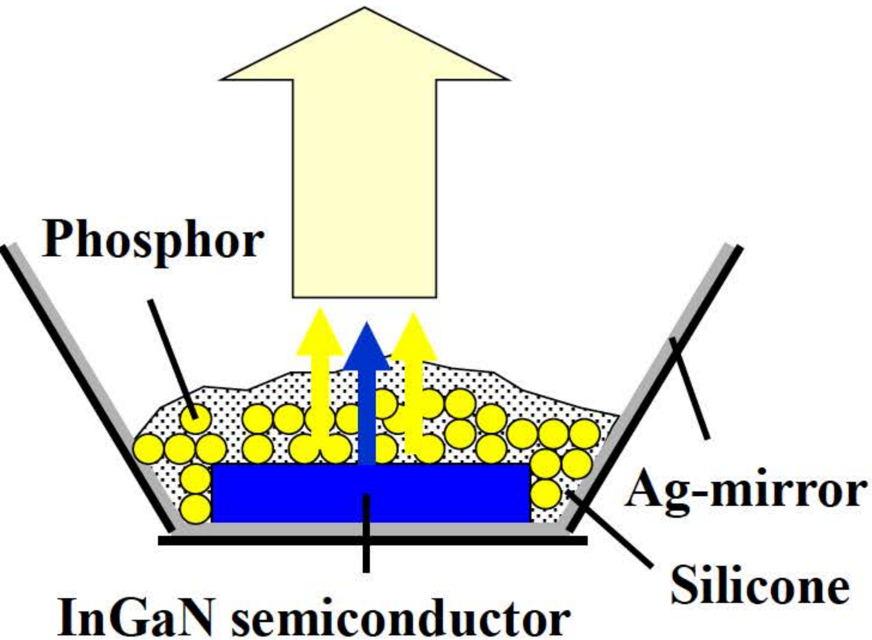


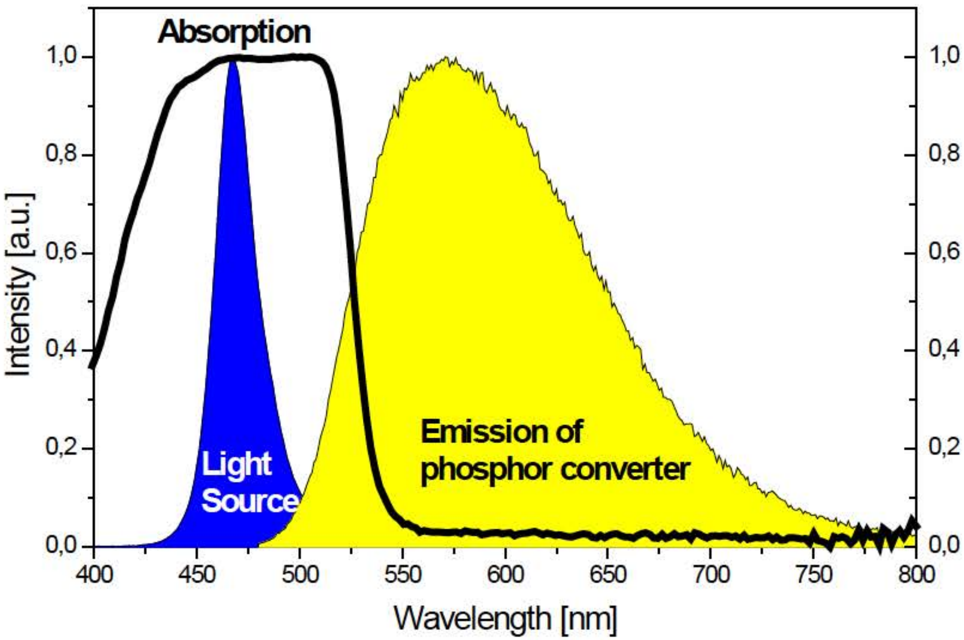
Blue (or UV) LED + Phosphors = White

Solid State Lighting

Display Backlight

Phosphor-LEDs



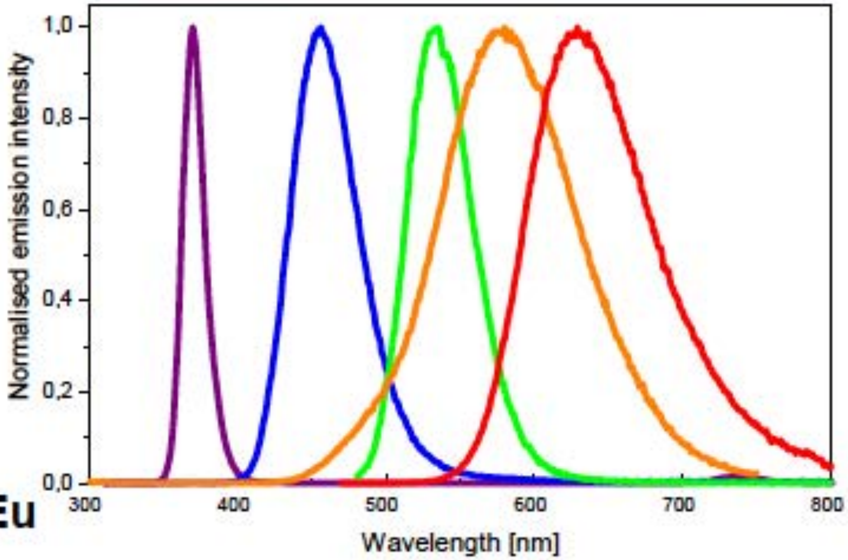


Blue LED chip:	**420 – 480 nm emitting (In,Ga)N LED**	
Phosphor layer:	**(1) Yellow**	**$T_c > 4000$ K „cool white“**
	(2) Yellow + red	**$T_c < 4000$ K „warm white“**
	(3) Green + red	**$2000\text{ K} < T_c < 8000\text{ K}$**
	(4) Red	**magenta colors**

Luminescent Materials (Phosphors)

Type of converter materials

1. Inorganic phosphors
   - Microscale powders
     - $SrYSi_4N_7:Ce$
     - $(Ba,Sr)_2SiO_4:Eu$
     - $(Ca,Sr,Ba)Si_2N_2O_2:Eu$
     - $SrYSi_4N_7:Eu$
     - (Y,Gd,Tb,Lu)AG:Ce
     - $CaAlSiN_3:Ce$
     - $(Ca,Sr)_2SiO_4:Eu$
     - (Ca,Sr)S:Eu
     - $(Ca,Sr,Ba)_2Si_5N_8:Eu$
     - $(Ca,Sr)AlSiN_3:Eu$
   - Nanoscale powders
     - (Y,Gd,Tb,Lu)AG:Ce
   - Quantum dots
     - (Zn,Cd)(S,Se), (In,Ga)(P,As),
2. Organic dyes
   - Polycyclic aromatic compounds
     - Perylenes
     - Coumarines
   - Metal complexes
     - Ln^{3+}-complexes Ln = Tm, Tb, Eu
     - Ru- and Ir-complexes



Requirements for Phosphors

General

- Strong absorption at the emission wavelength of the semiconductor-LED
  → spin-and parity-allowed transition, e.g. $4f^n - 4f^{n-1}5d^1$
- Quantum yield > 90%
- Stability with respect to O_2, CO_2 and H_2O
- Stability at high excitation density (100 - 200 W/cm^2)
- Compatibility with the LED production process

Blue + yellow (1st approach)

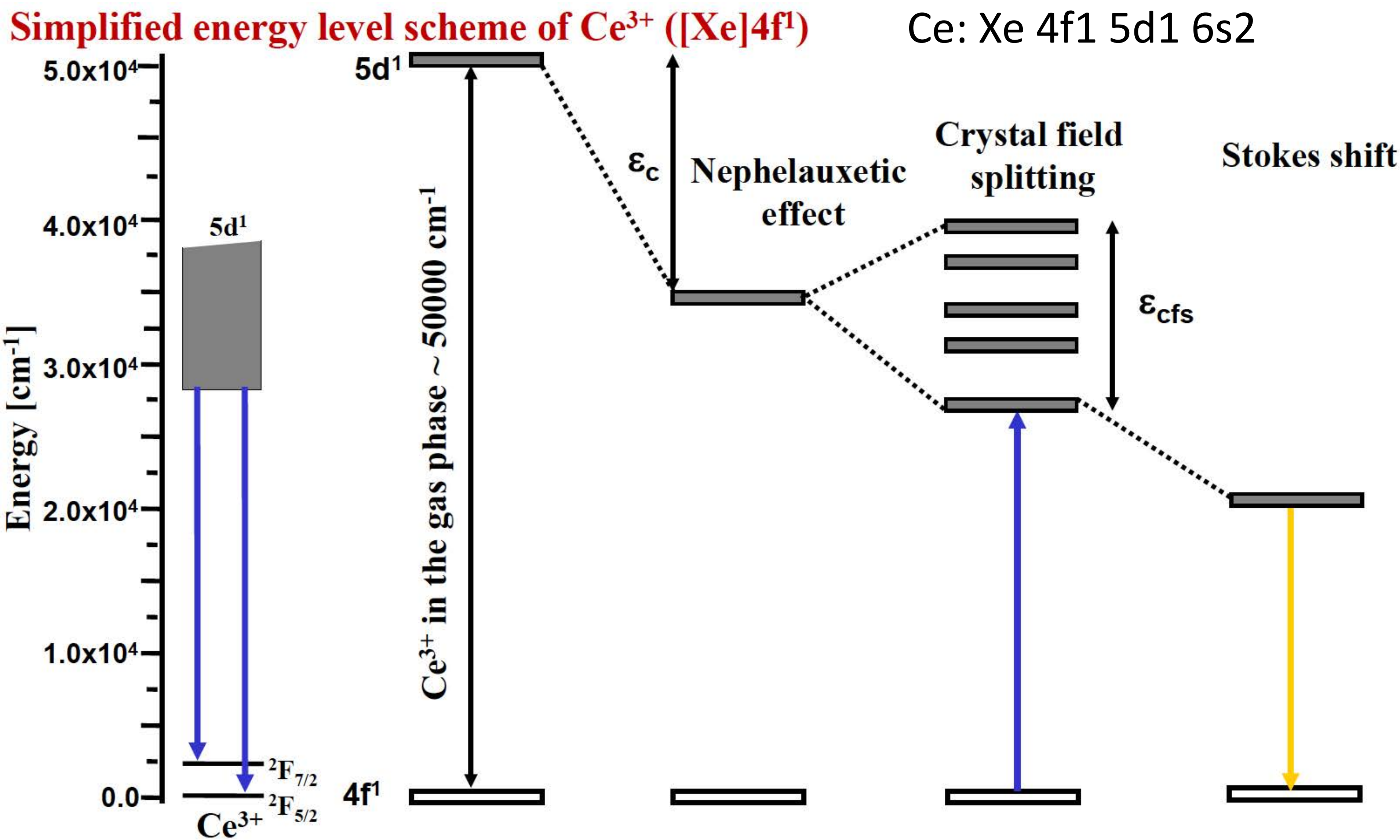
- Broad emission band between 560 - 580 nm
  → Ce^{3+}- phosphors (splitting of the ground state $^2F_{5/2}$ + $^2F_{7/2}$)

Blue + green/yellow + red (2nd and 3rd approach)

• Green / yellow phosphor →	Eu^{2+} or Ce^{3+}	530 - 560 nm
• Red phosphor →	Eu^{2+}	590 - 620 nm

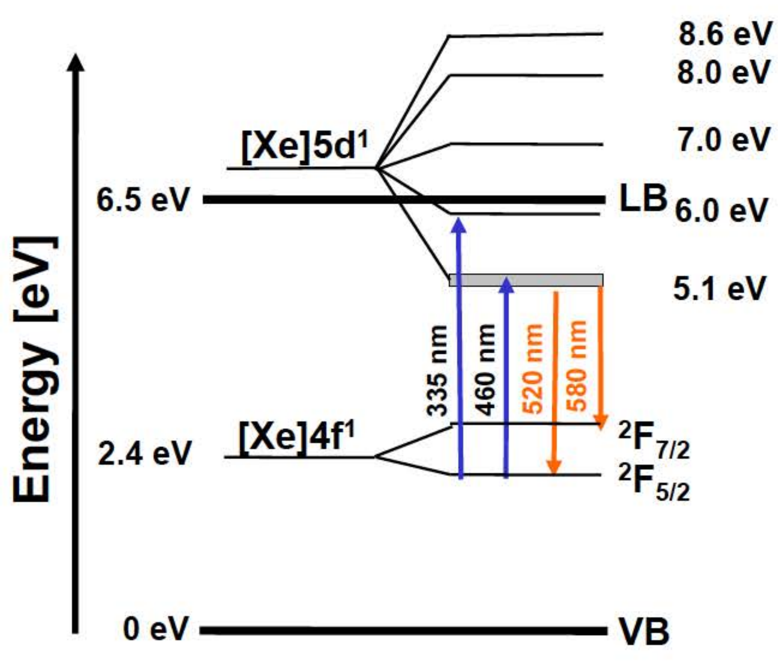
Ce^{3+} Phosphors

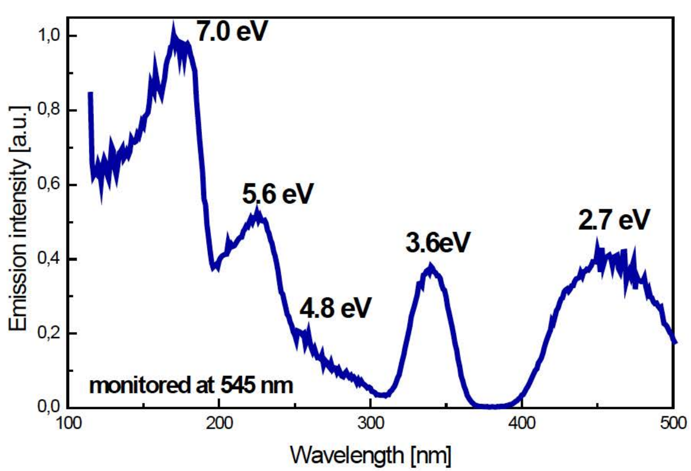
Ce: Xe 4f1 5d1 6s2

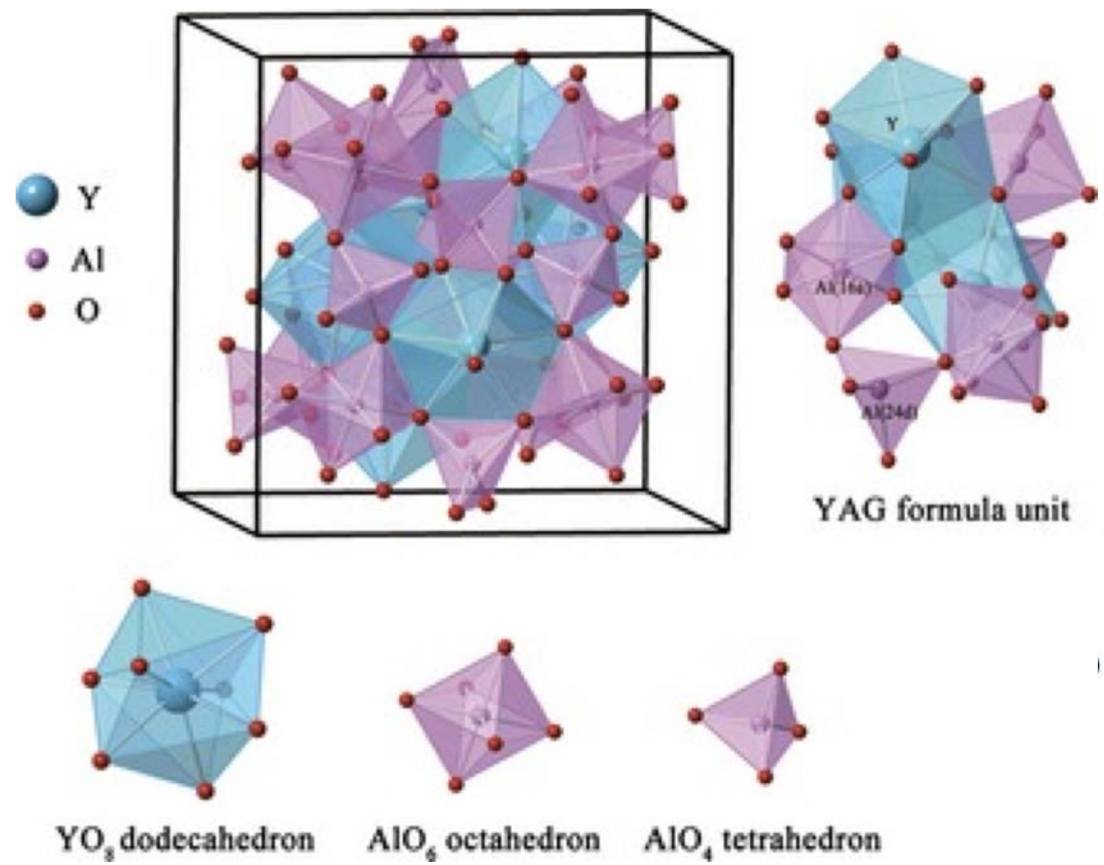


Ce^{3+} Phosphors

Energy levels and excitation spectrum of Ce^{3+} in $Y_3Al_5O_{12}$







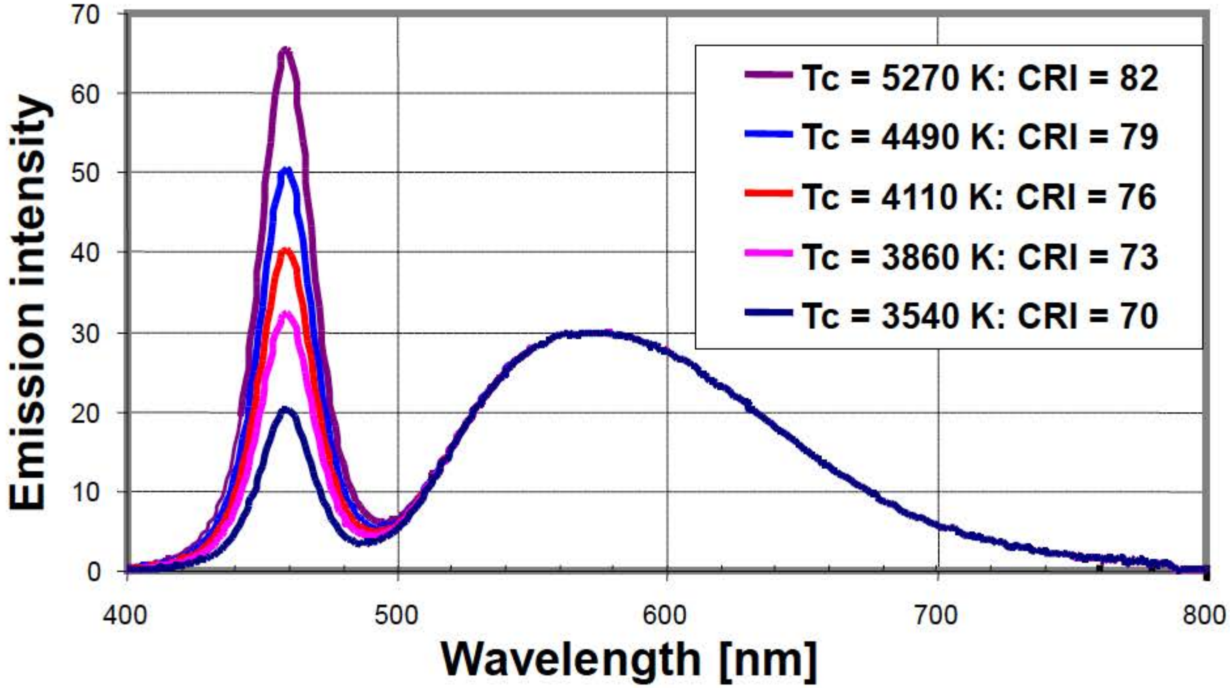
Yttrium aluminium garnet (YAG, $Y_3Al_5O_{12}$) is a synthetic crystalline material of the garnet group.

Ce^{3+} Phosphors

Host lattice	λ_{abs} [nm]	λ_{em} [nm]	ε_{cfs} [cm^{-1}]	ε_c [cm^{-1}]
$SrAl_{12}O_{19}$	224, 235, 244, 252, 261	290, 315	6300	10000
$LaPO_4$	203, 225, 238, 250, 323	320, 335	11900	8700
$LaMgAl_{11}O_{19}$	220, 232, 243, 255, 270	345	8400	10000
YPO_4	203, 225, 238, 250, 323	335, 355	18000	9600
$YAlO_3$	219, 237, 275, 291, 303	370	12700	12900
$LuAlO_3$	216, 230, 275, 292, 308	370	12650	13800
$LaMgB_5O_{10}$	202, 225, 239, 257, 272	385, 410	9000	12700
YBO_3	219, 245, 338, 357	390, 415	17600	13300
Lu_2SiO_5	205, 215, 267, 296, 356	405, 420	20700	12300
$Lu_3Al_5O_{12}$	205, 225, 265, 350, 445	525, 540		
$Y_3Al_5O_{12}$	205, 225, 261, 340, 458	545, 555	27000	14700

Optically Pumped White LEDs

Blue (In,Ga)N chip + $(Y,Gd)_3Al_5O_{12}$:Ce



The first commercially available LEDs followed this approach (1)

- **Color rendering CRI = 70 – 85**
- **Cool white light**
- **Luminous efficiency up to 303 lm/W**
- **Problem: Low color rendering for red color and low color temperature**

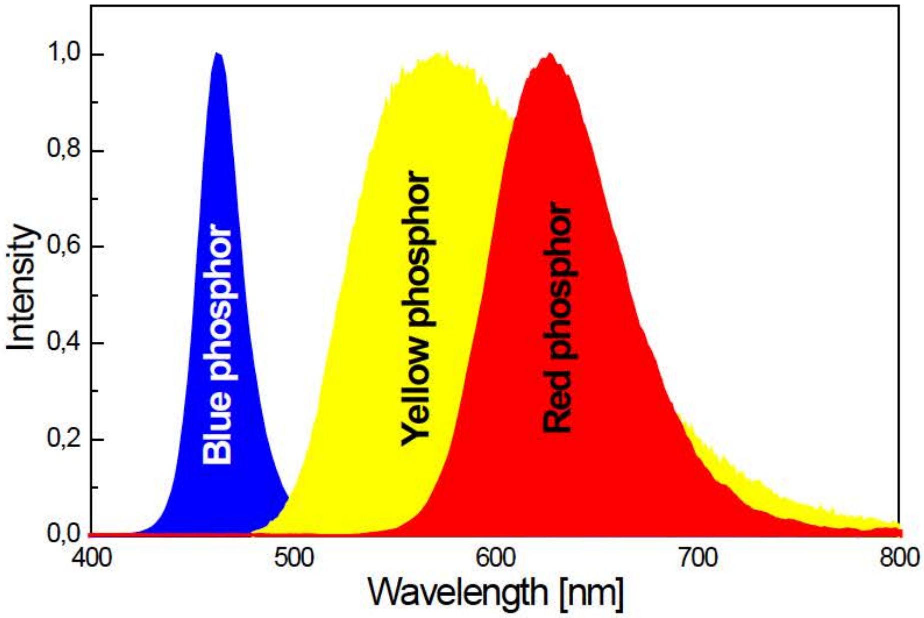
Optically Pumped White LEDs

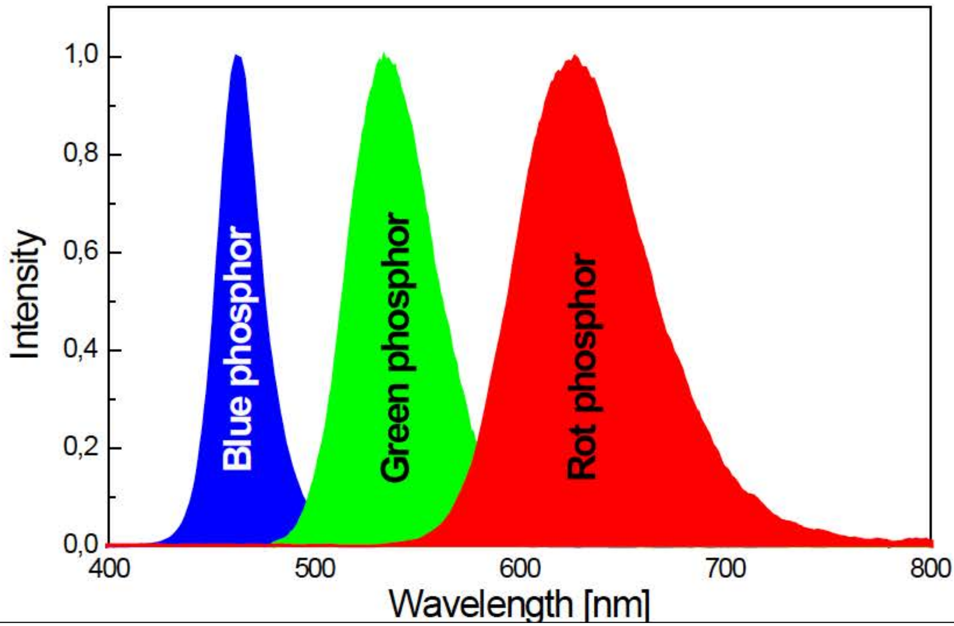
White pcLEDs with high color rendering

(1) Blue LED + $(Y,Gd)_3Al_5O_{12}$ ⇒ **CRI > 75 only for T_c > 4000 K**

(2) Blue LED + $(Y,Gd)_3Al_5O_{12}$ + red ⇒ **CRI > 85 for T_c < 4000 K**

(3) Blue LED + green + red ⇒ **CRI > 85 for 2700 < T_c < 8000 K**





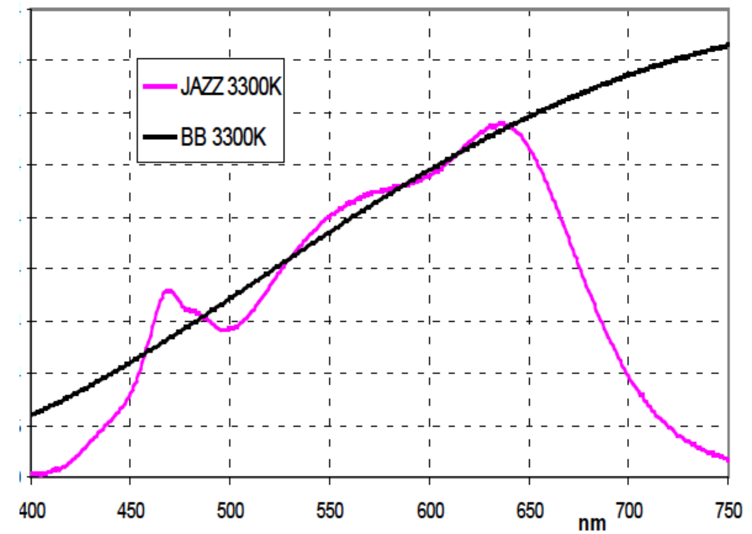
Optically Pumped White LEDs

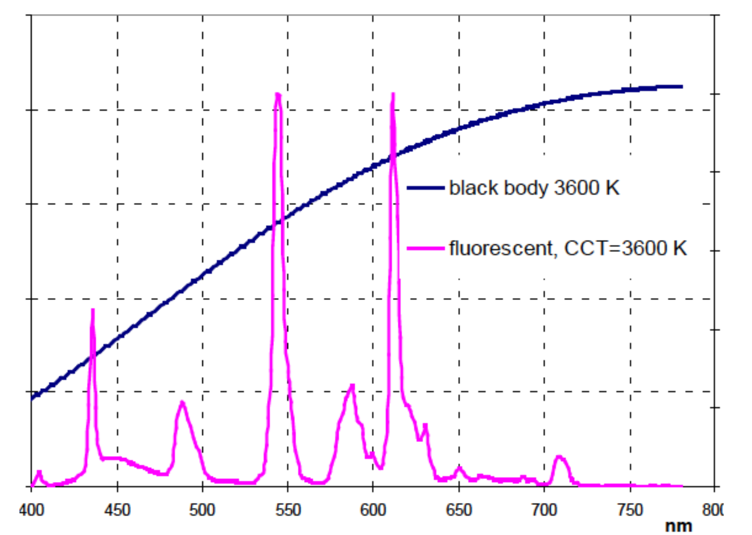
White pcLEDs with high color rendering

Light sources for general lighting require high color rendering even at low color temperatures

2nd Approach

- **$(Y,Gd)_3Al_5O_{12}$ + red phosphor**
- **CRI = 85 - 95**
- **T_c = 2800 to 4000 K**
- **1 W LEDs**
- **20 - 25 lm at 350 mA**
- **Reduced luminous flux (30 – 40%)**





Problems of Ce^{3+} Phosphors

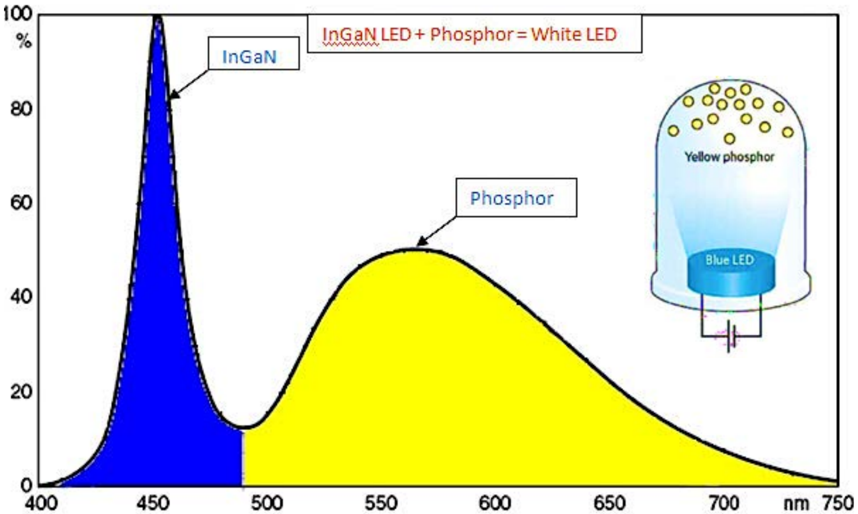
General properties

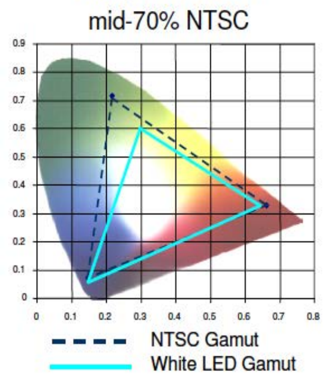
- Relatively narrow absorption bands
- Relatively broad emission band
- Ce^{3+}-phosphors with red emission and high thermal quenching temperature are not known

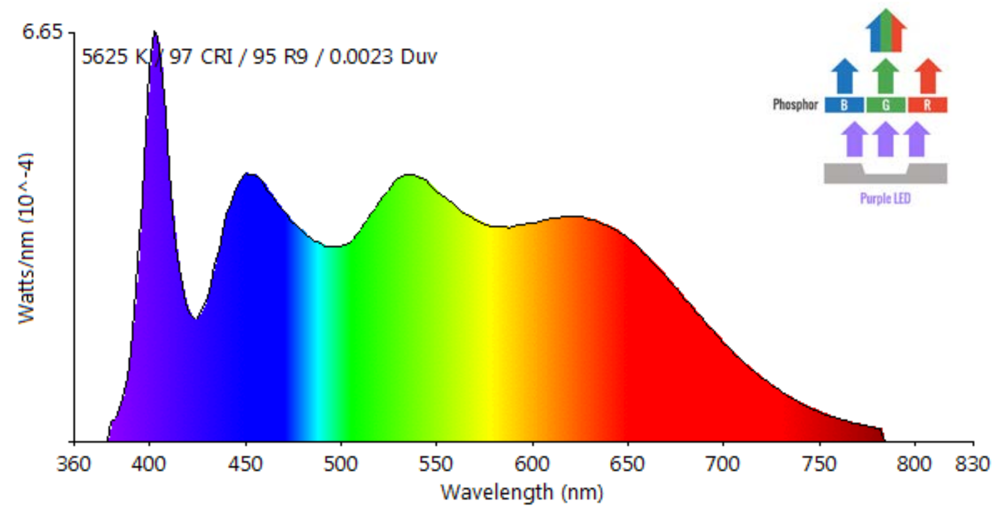
Alternative activators for red-emitting phosphors

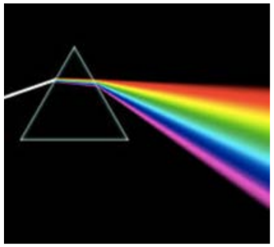
Activator	Spectral range [nm]	Lumen equivalent [lm/W_{opt}]	Decay time τ	Efficiency	Absorption at 450 nm
Eu^{2+}	360 - 700	50 – 550	~ 1 µs	high	strong
Eu^{3+}	590 - 710	200 – 360	~ 1 ms	high	weak
Sm^{2+}	670 - 770	< 100	~ 1 µs	high	moderate
Sm^{3+}	560 - 710	240 – 260	0.5 ms	moderate	weak
Pr^{3+}	590 - 680	100 – 220	0.1 ms	moderate - high	weak
Mn^{2+}	500 - 650	100 - 550	5-15 ms	high	weak
Mn^{4+}	620 - 680	80 – 230	1-10 ms	high	moderate
Cr^{3+}	680 - 750	< 100	1-10 ms	high	moderate
Fe^{3+}	> 700	< 50	5-15 ms	medium	weak

The Future of WLEDs









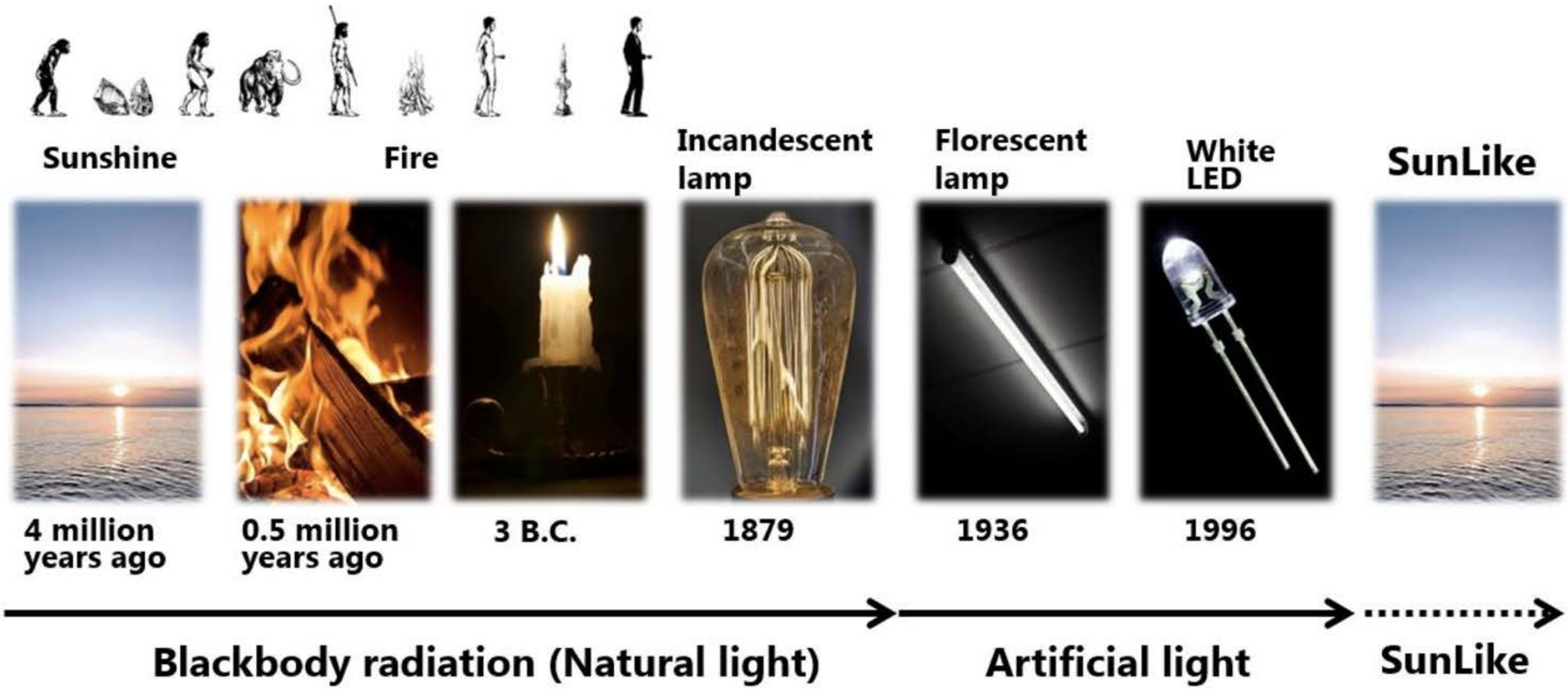
Blue LED + Yellow Phosphor:

- Poor color rendering
- Circadian rhythms disruption
- Suppression of melatonin

An ideal phosphor:

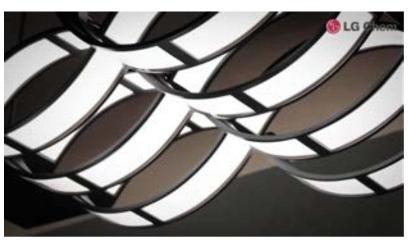
- Near-unity PLQE
- Good spectral overlapping
- Excellent thermal and photo-stability
- Great color rendering

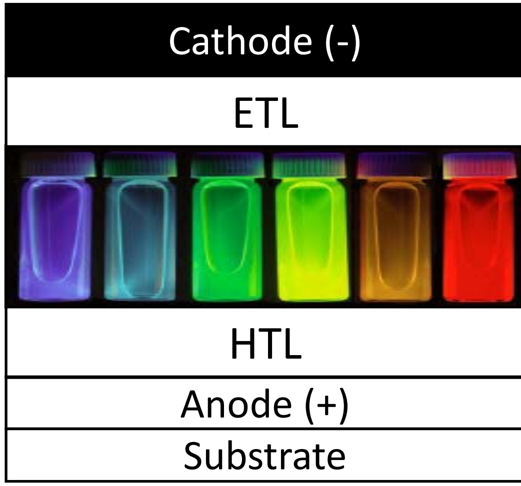
Solid State Lighting

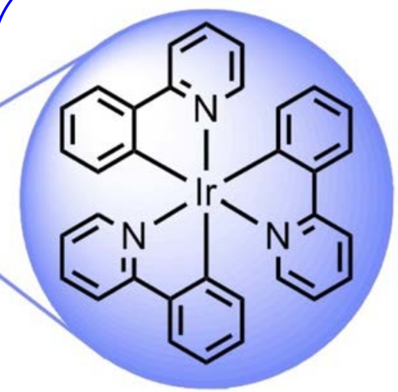


Courtesy of Seoul Semiconductor

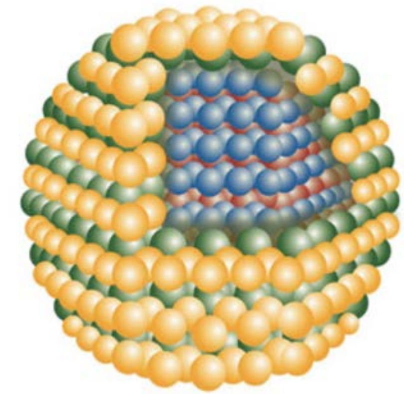
Electrically Driven Thin Film LEDs



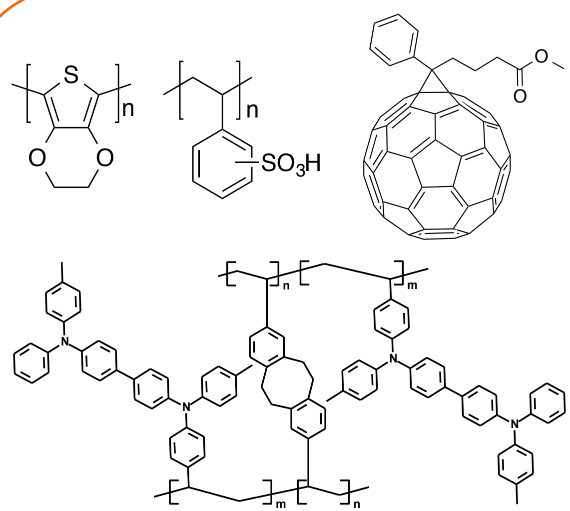




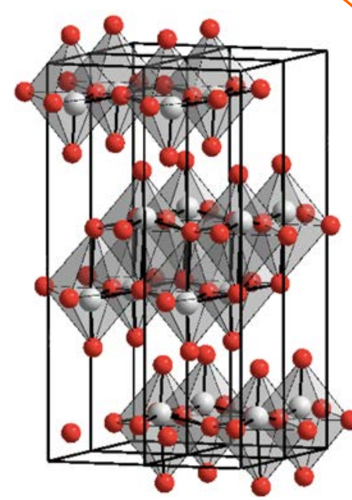
Phosphorescent Metal Complexes



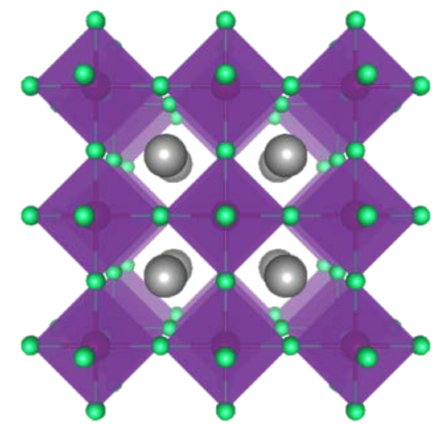
Colloidal Quantum Dots



Organic Charge Transport Materials



Metal Oxides



Perovskite Materials

Organic Light Emitting Diodes

What is OLEDs?

Viable Candidates for:

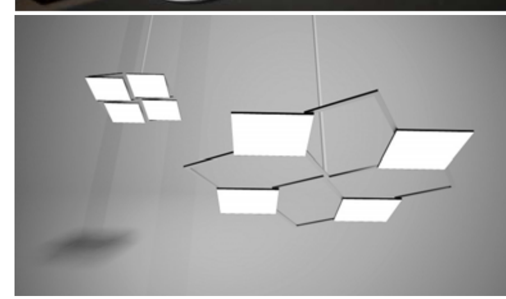
New generation flat full color displays

Superior to current LCD displays:

•Compact size
•Broader viewing angle
•Bright saturated colors
•Faster response
•More power efficiency
•Can be flexible and transparent

Illumination sources (white OLEDs)

•High power efficiency (2 to 3 times > incandescent lamp)
•Generate pleasing white light with high CRI
•Enable "designer color" on demand
•Provide new design opportunities for architects.



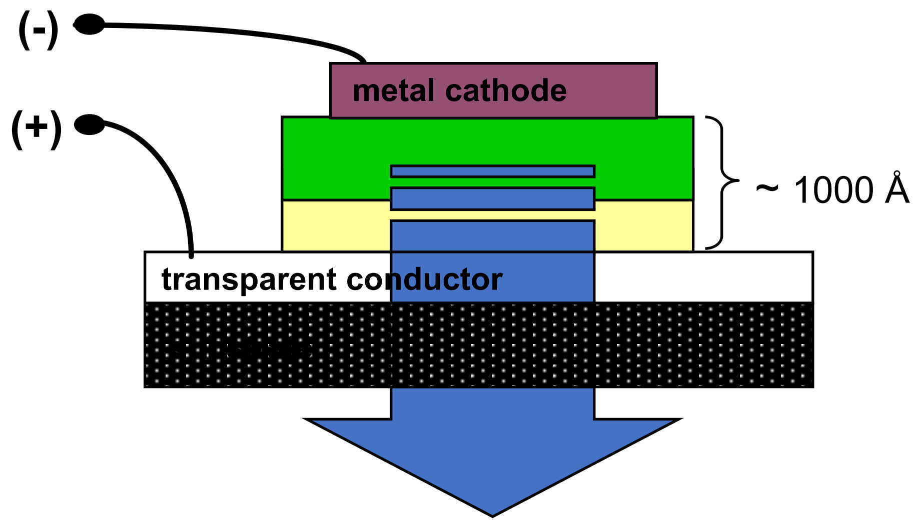
What is OLEDs?

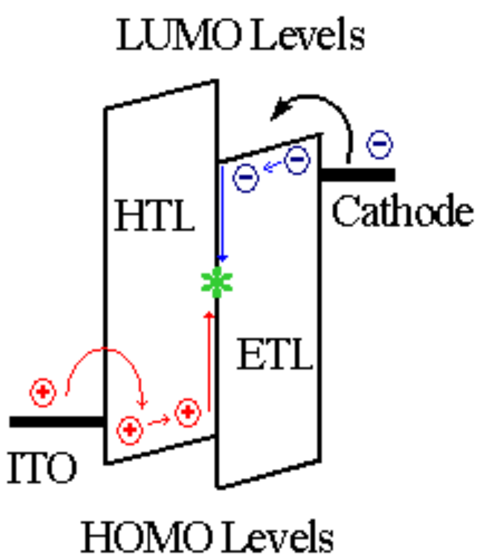
The structure

- About 1000Å organic layers sandwiched between 2 electrodes
- At least 1 electrode is transparent

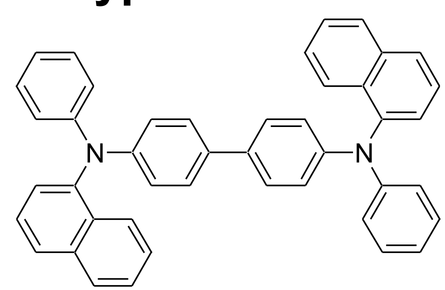
Operation principle

- Charge carriers injection
- Migration
- Recombination
- **Electroluminescence**



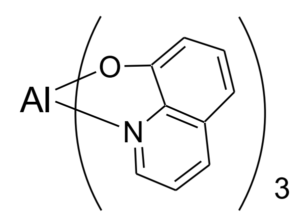


Typical HTL:



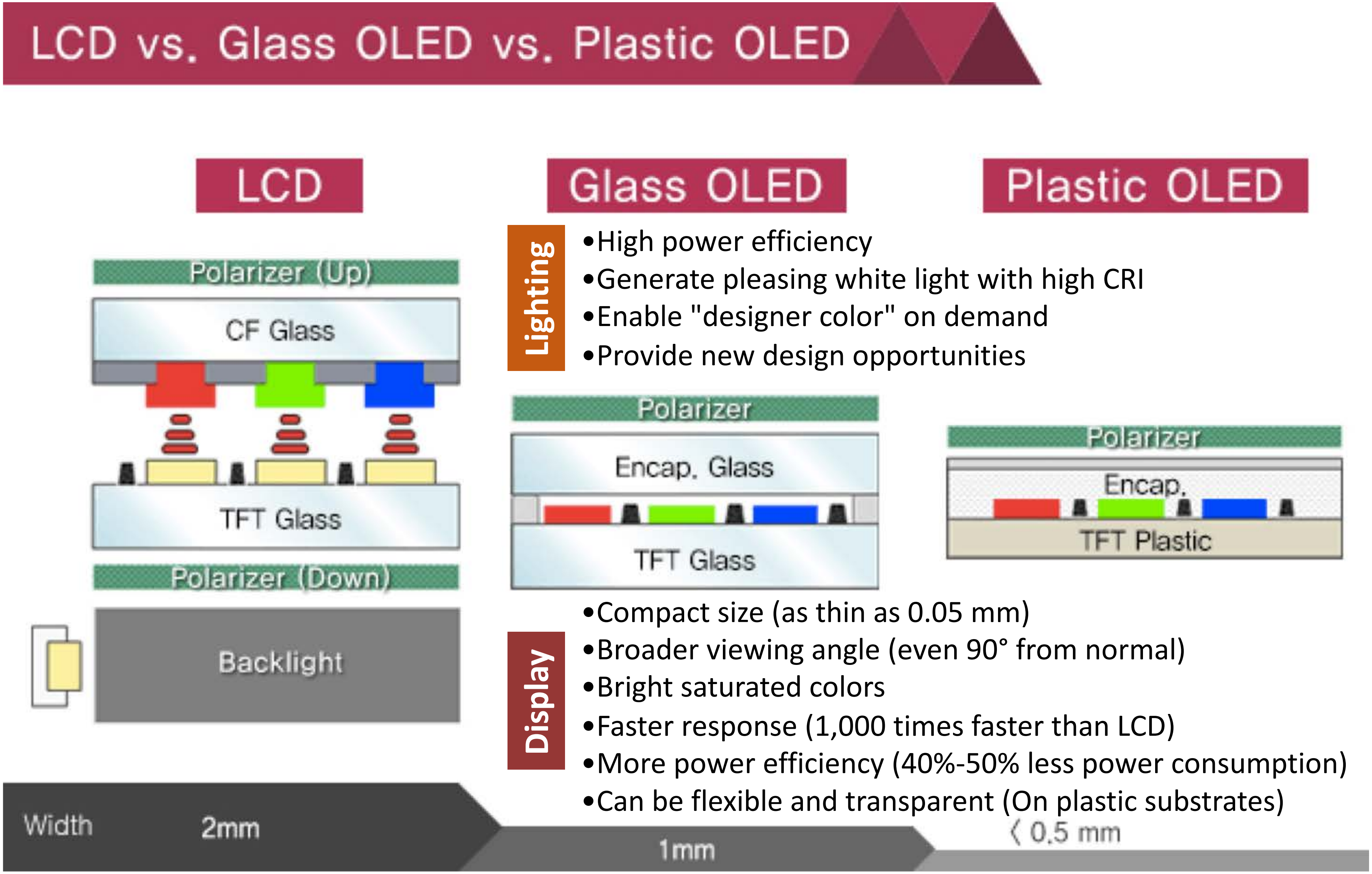
α-NPD

Typical ETL:



Alq_3

Why OLEDs?



Lighting

- High power efficiency
- Generate pleasing white light with high CRI
- Enable "designer color" on demand
- Provide new design opportunities

Display

- Compact size (as thin as 0.05 mm)
- Broader viewing angle (even 90° from normal)
- Bright saturated colors
- Faster response (1,000 times faster than LCD)
- More power efficiency (40%-50% less power consumption)
- Can be flexible and transparent (On plastic substrates)

The First Efficient OLED

Organic electroluminescent diodes

C. W. Tang and S. A. VanSlyke
Research Laboratories, Corporate Research Group, Eastman Kodak Company, Rochester, New York 14650

(Received 12 May 1987; accepted for publication 20 July 1987)

A novel electroluminescent device is constructed using organic materials as the emitting elements. The diode has a double-layer structure of organic thin films, prepared by vapor deposition. Efficient injection of holes and electrons is provided from an indium-tin-oxide anode and an alloyed Mg:Ag cathode. Electron-hole recombination and green electroluminescent emission are confined near the organic interface region. High external quantum efficiency (1% photon/electron), luminous efficiency (1.5 lm/W), and brightness (> 1000 cd/m^2) are achievable at a driving voltage below 10 V.

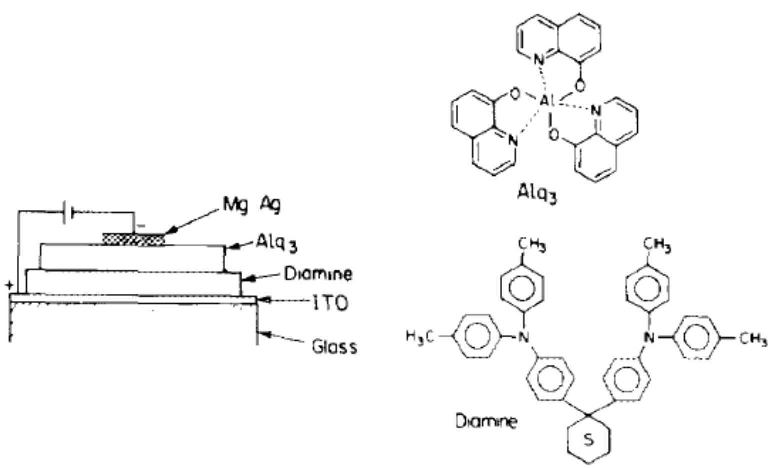


FIG. 1. Configuration of EL cell and molecular structures.

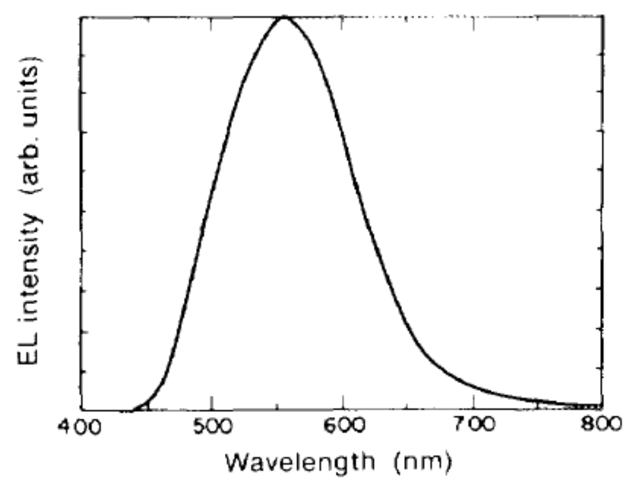
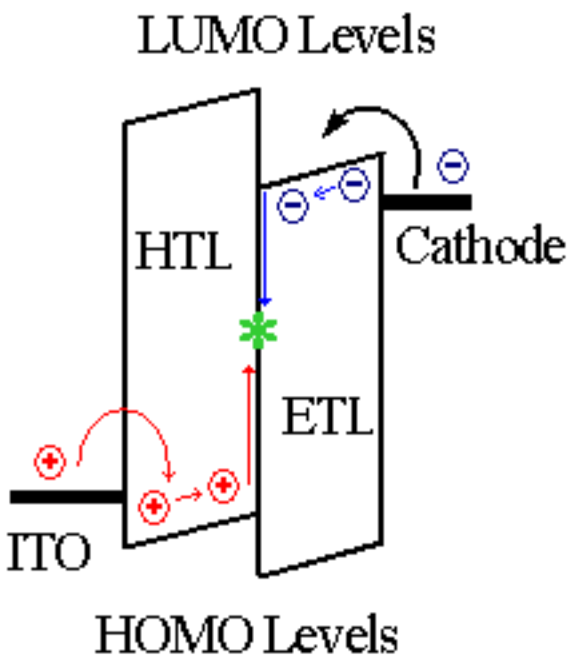


FIG. 3. Electroluminescence spectrum of ITO/diamine/Alq$_3$/Mg:Ag.

Cited 16591 times

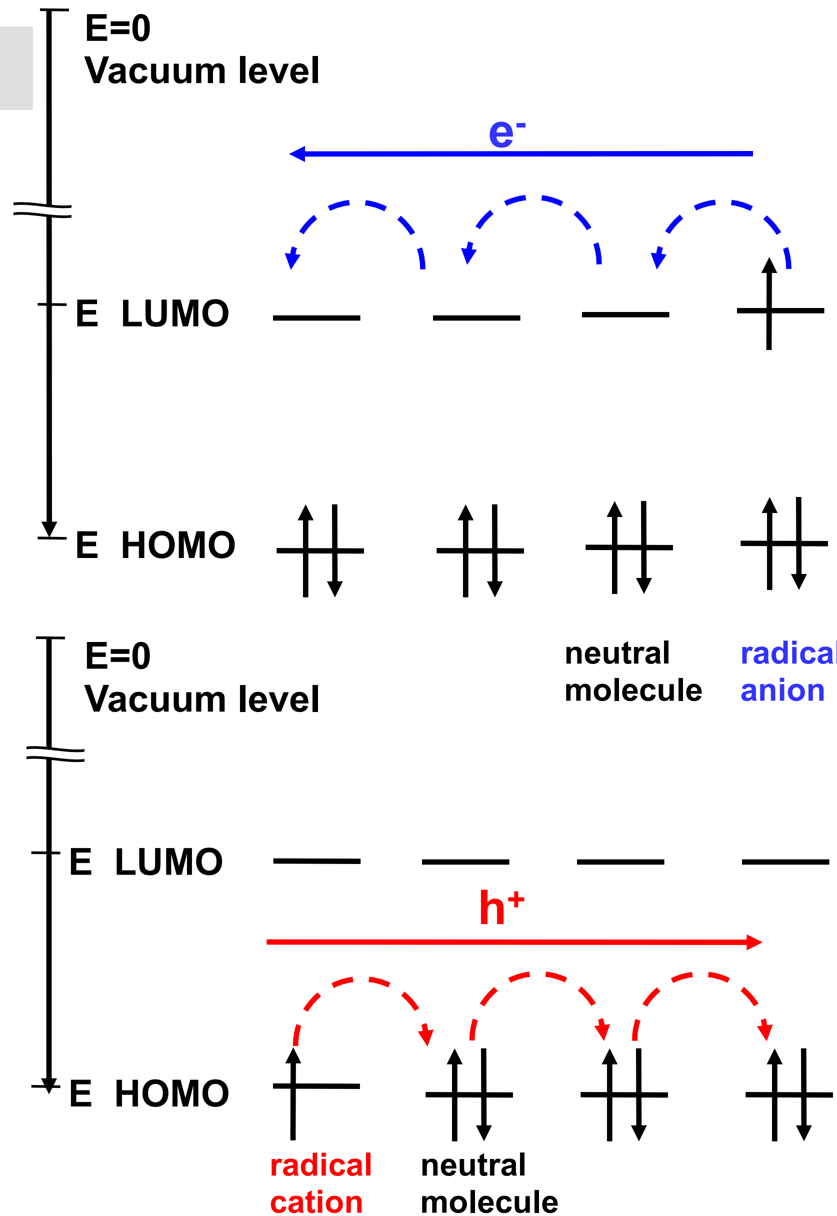
How OLEDs work?

Lowest **U**noccupied **M**olecular **O**rbital



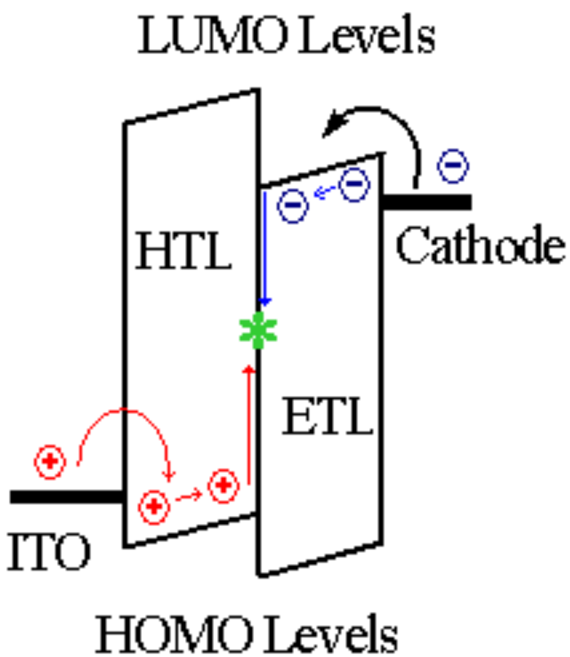
Highest **O**ccupied **M**olecular **O**rbital

- **LUMO of ETL transport electrons;**
- **HOMO of HTL transport holes.**

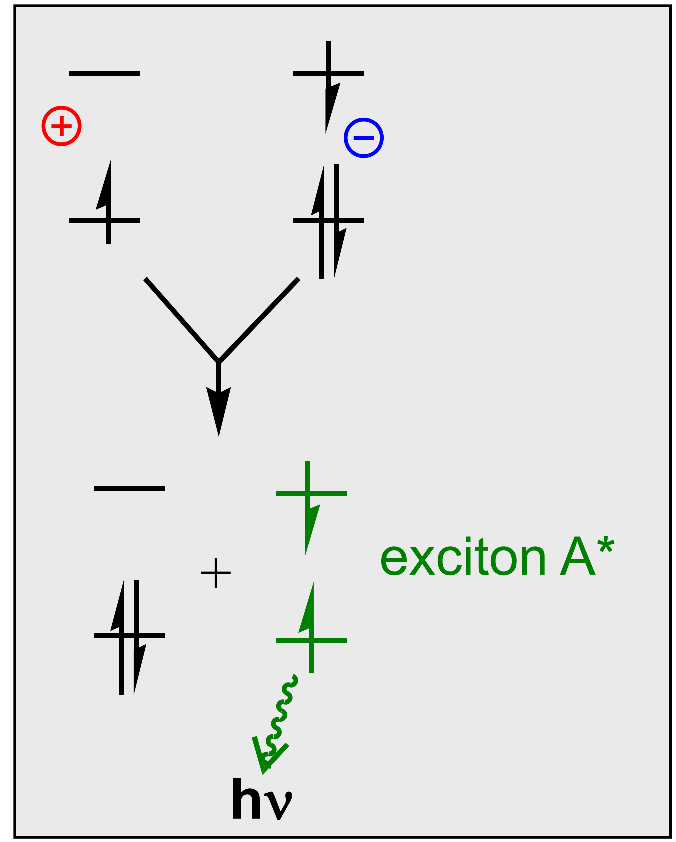


How OLEDs work?

Lowest **U**noccupied **M**olecular **O**rbital



Highest **O**ccupied **M**olecular **O**rbital

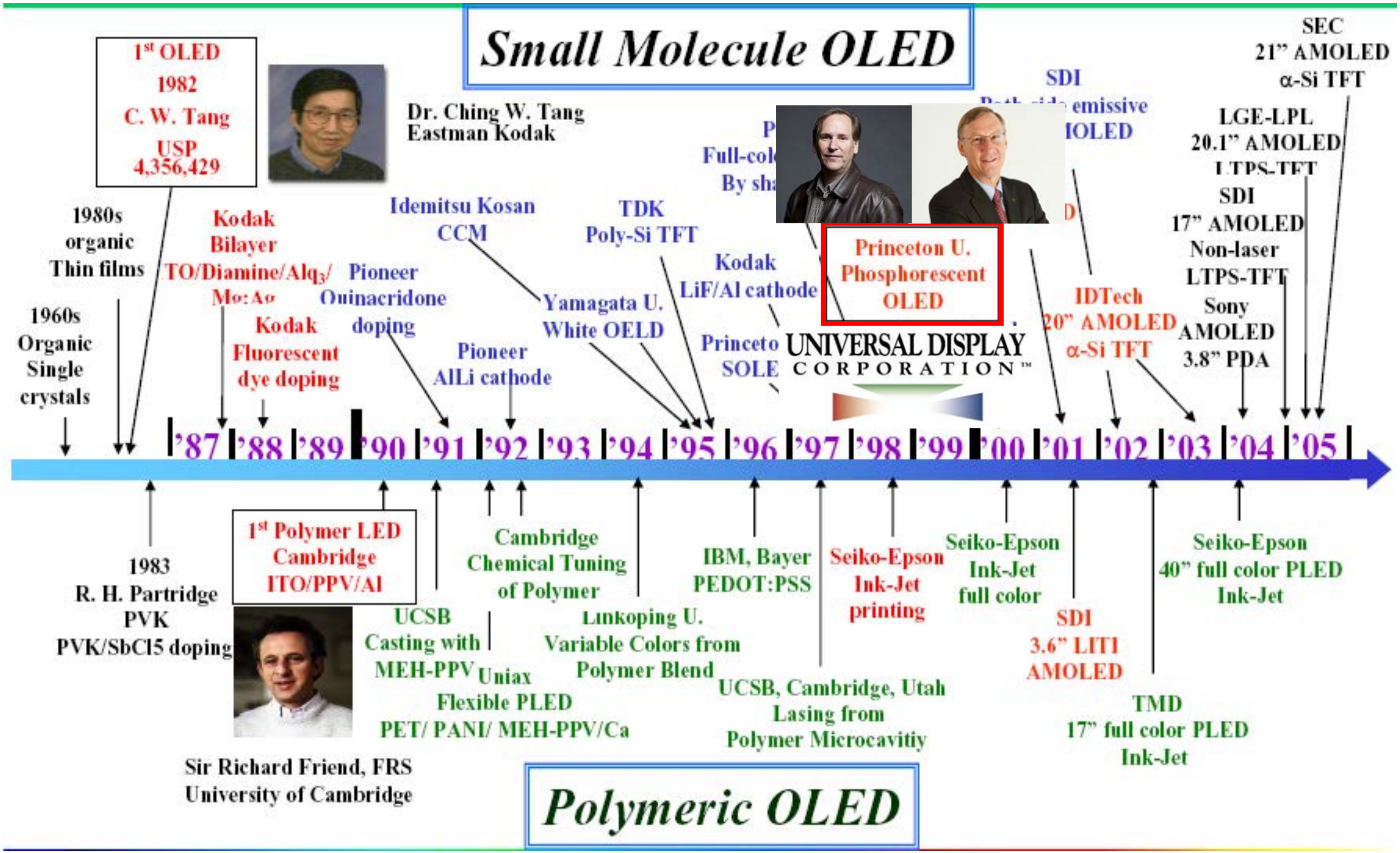


The emission color is proportional to the $\Delta E_{HOMO\text{-}LUMO}$ of emissive materials (exciton).

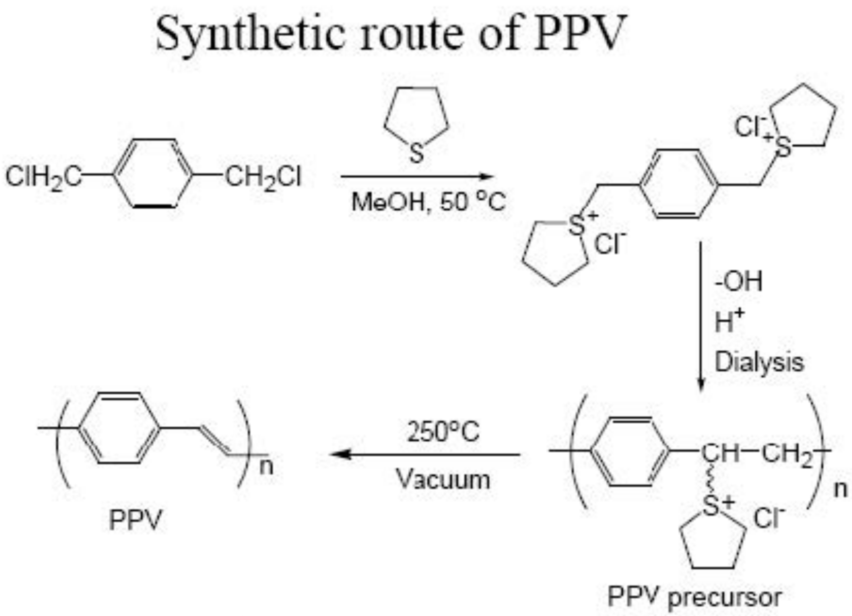
$$A^* \rightarrow A + h\nu$$

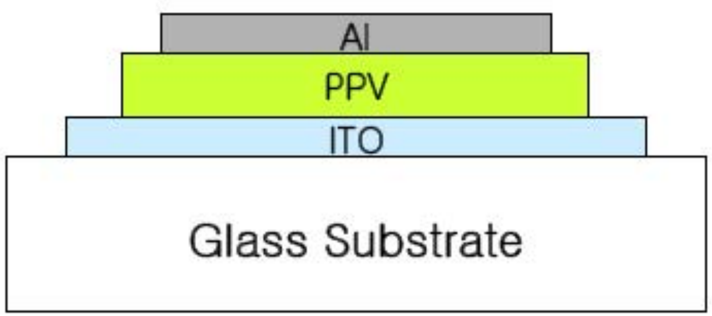
$$\Delta E_{HOMO\text{-}LUMO} \sim h\nu$$

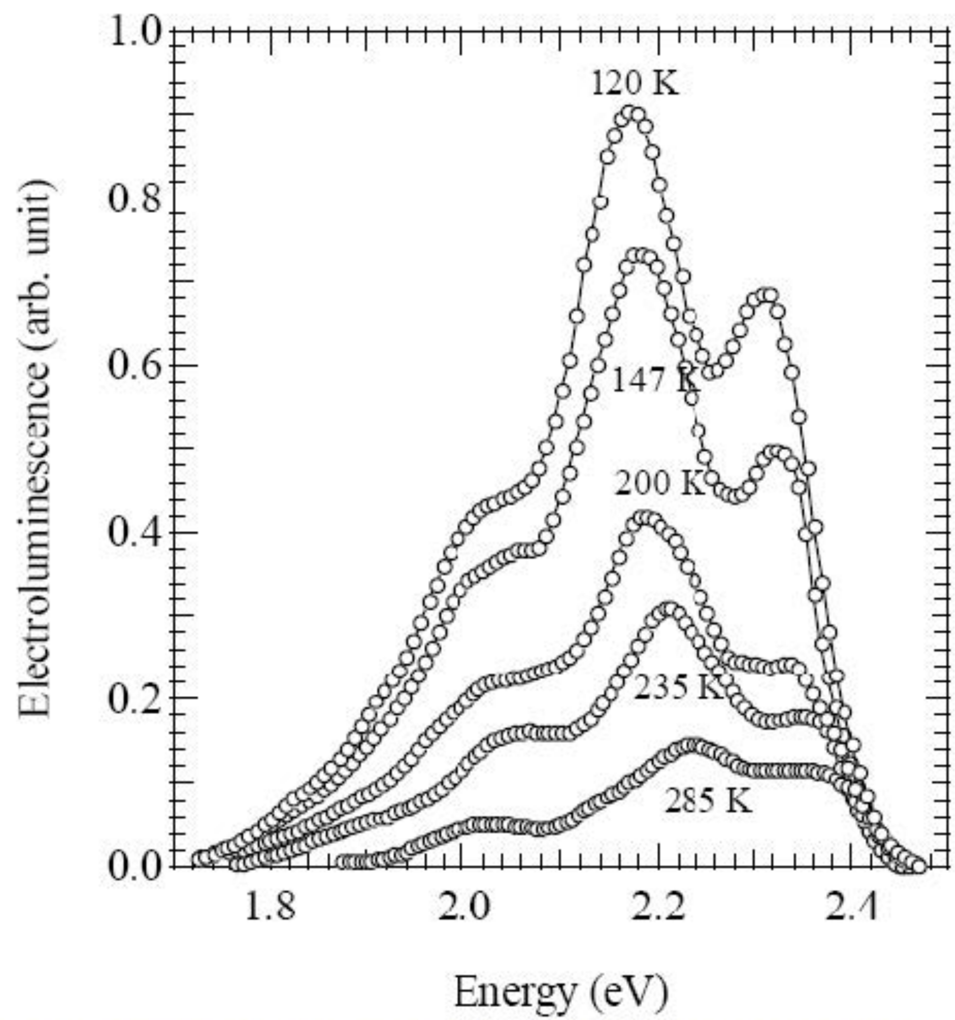
Early Development of OLEDs



The First Polymer LEDs



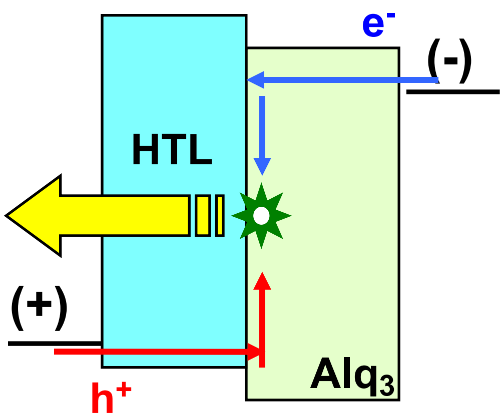


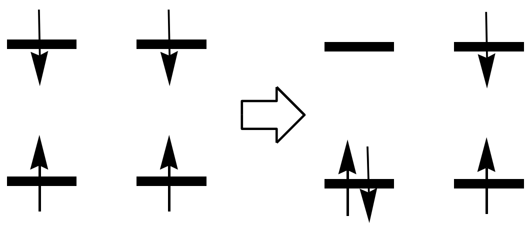


J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, Nature **347**, 539 (1990).

Cited 13681 times

Doped emissive layer (EL).



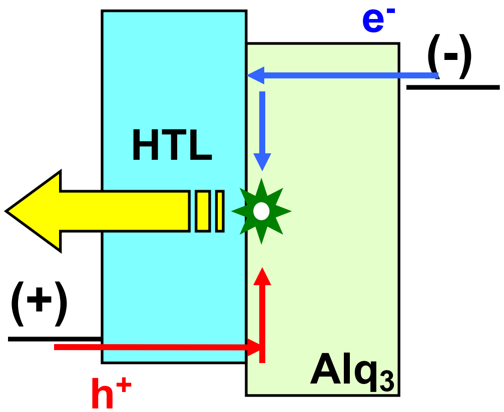


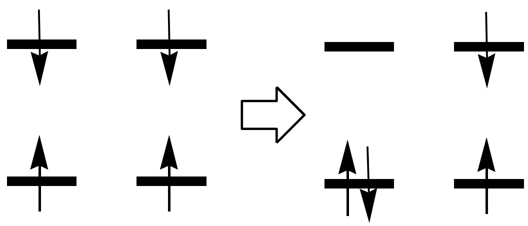
$$Alq_3^* + Alq_3^* \longrightarrow Alq_3 + Alq_3^*$$

Problem:
excitons emit from a dense, pure matrix: significant self-quenching is typical

Efficiency is ~ 1%

Doped emissive layer (EL).





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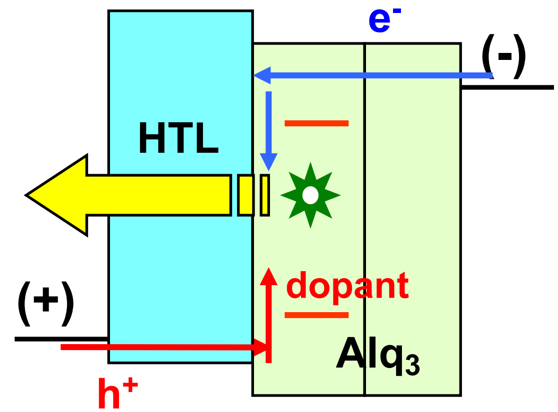
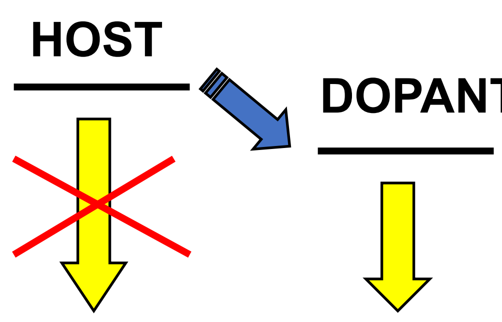


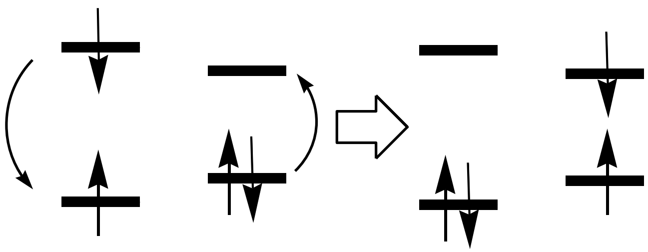
Doping (0.5-1%) fluorescent dyes in the emissive layer

Efficiency is ~ 2-3 %

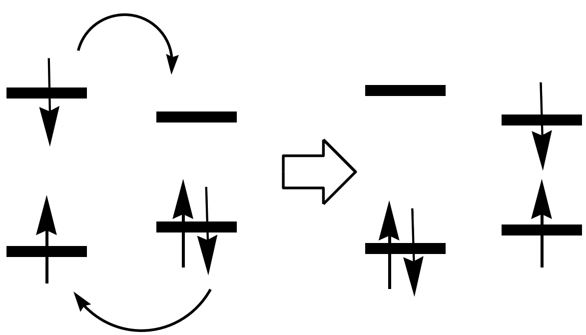


Doped emissive layer (EL).

Förster energy transfer

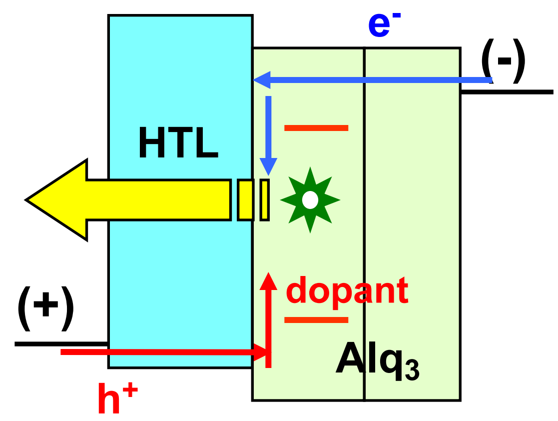


Dexter energy transfer



Advantage:
Self-quenching of excitons is prevented.

Tune the color of OLEDs by controlling emission energies of dopants.



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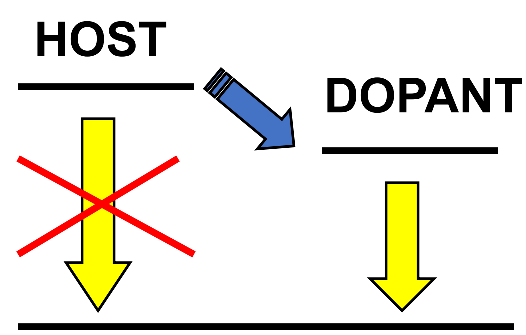
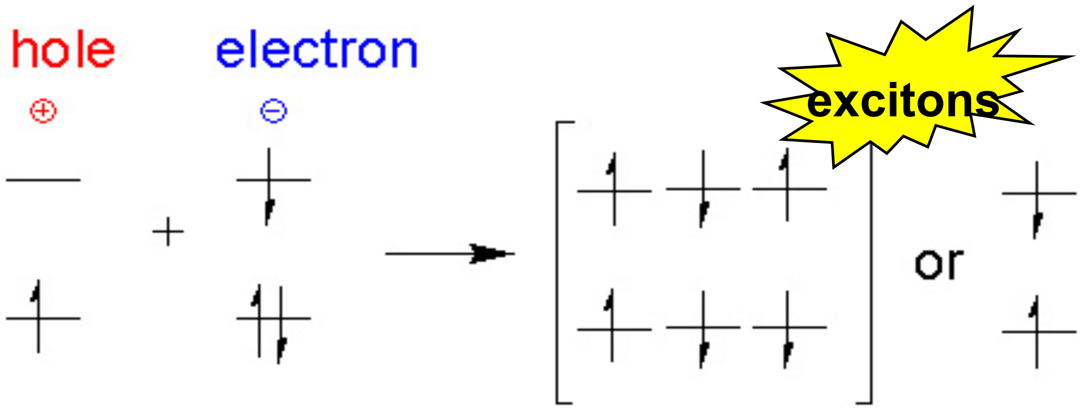
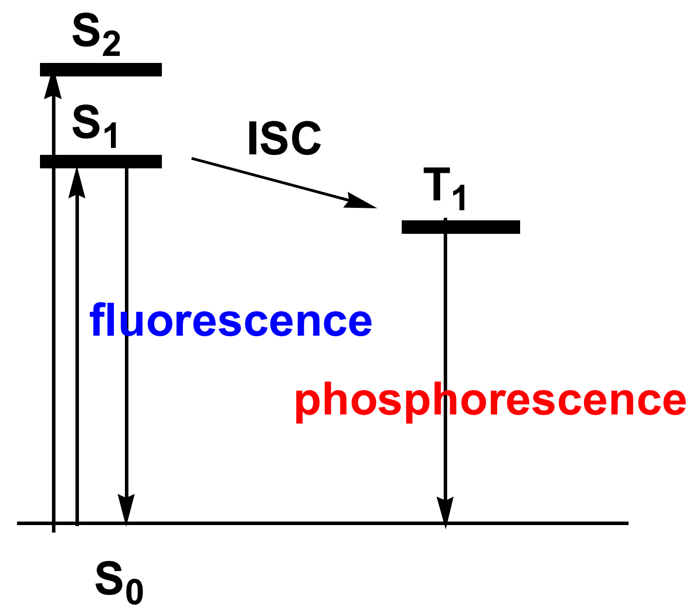
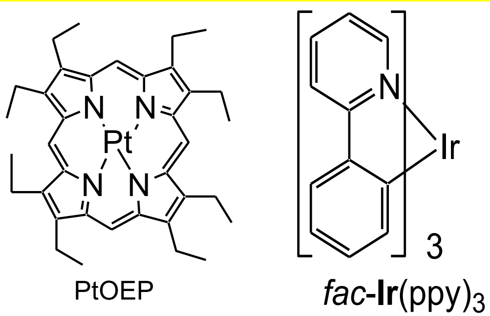


Electrophosphorescence







Heavy metal Ir and Pt complexes facilitate intersystem crossing

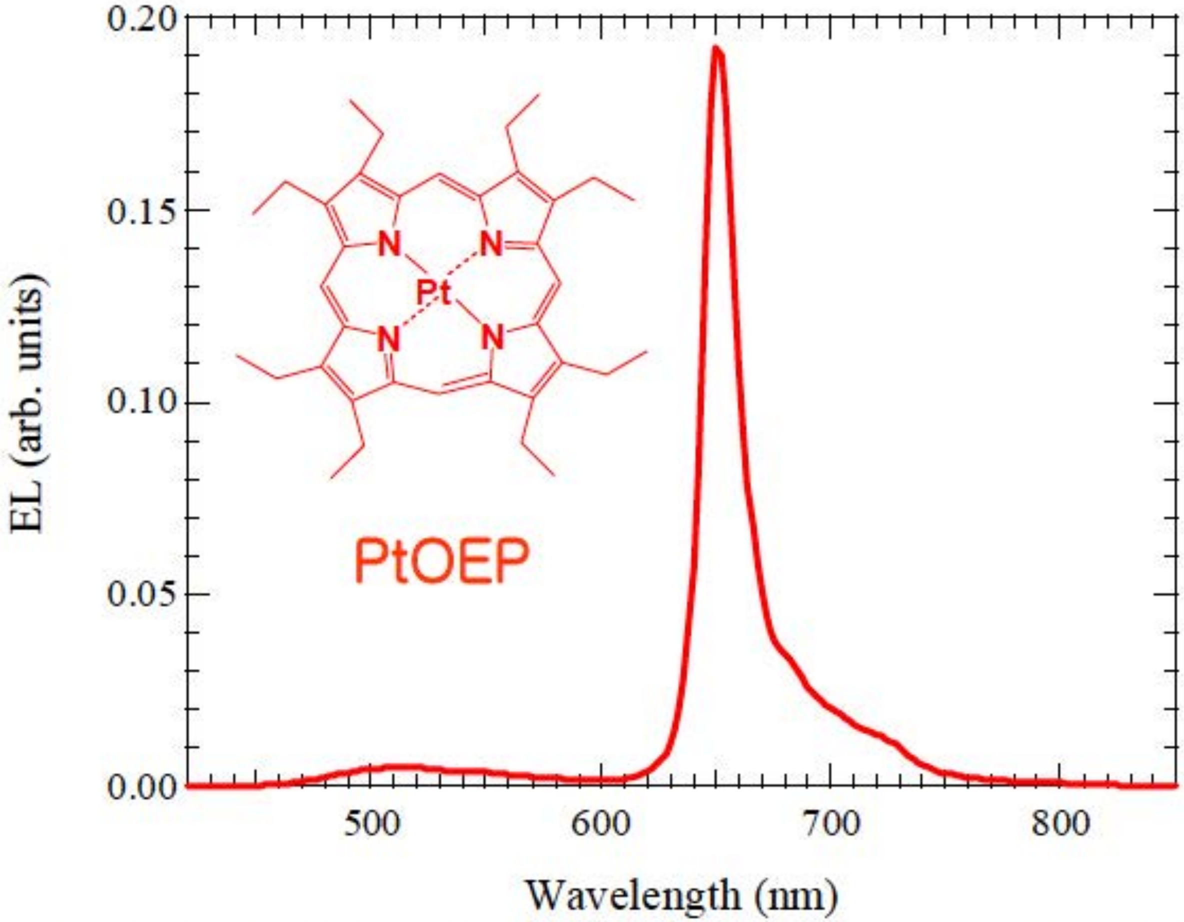
Harvested only by phosphorescent lumophores

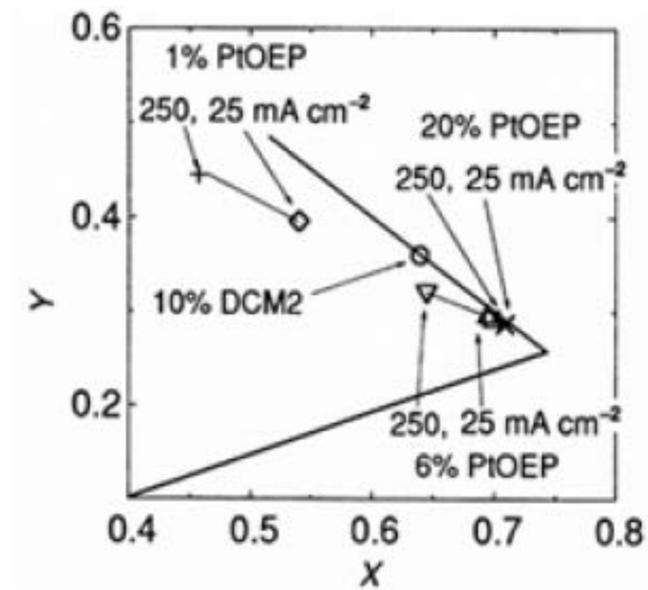
Harvested both by fluorescent and phosphorescent dyes

•Experimentally determined singlet fraction for Alq_3 based OLEDs = 22±3% Baldo *et.al.*, *Phys. Rev. B* ,**1999**

Max theoretical quantum efficiency	Fluorescent	Phosphorescent
Internal	**25%**	**100%**
External	**5%**	**20%**

The First Phosphorescent OLED



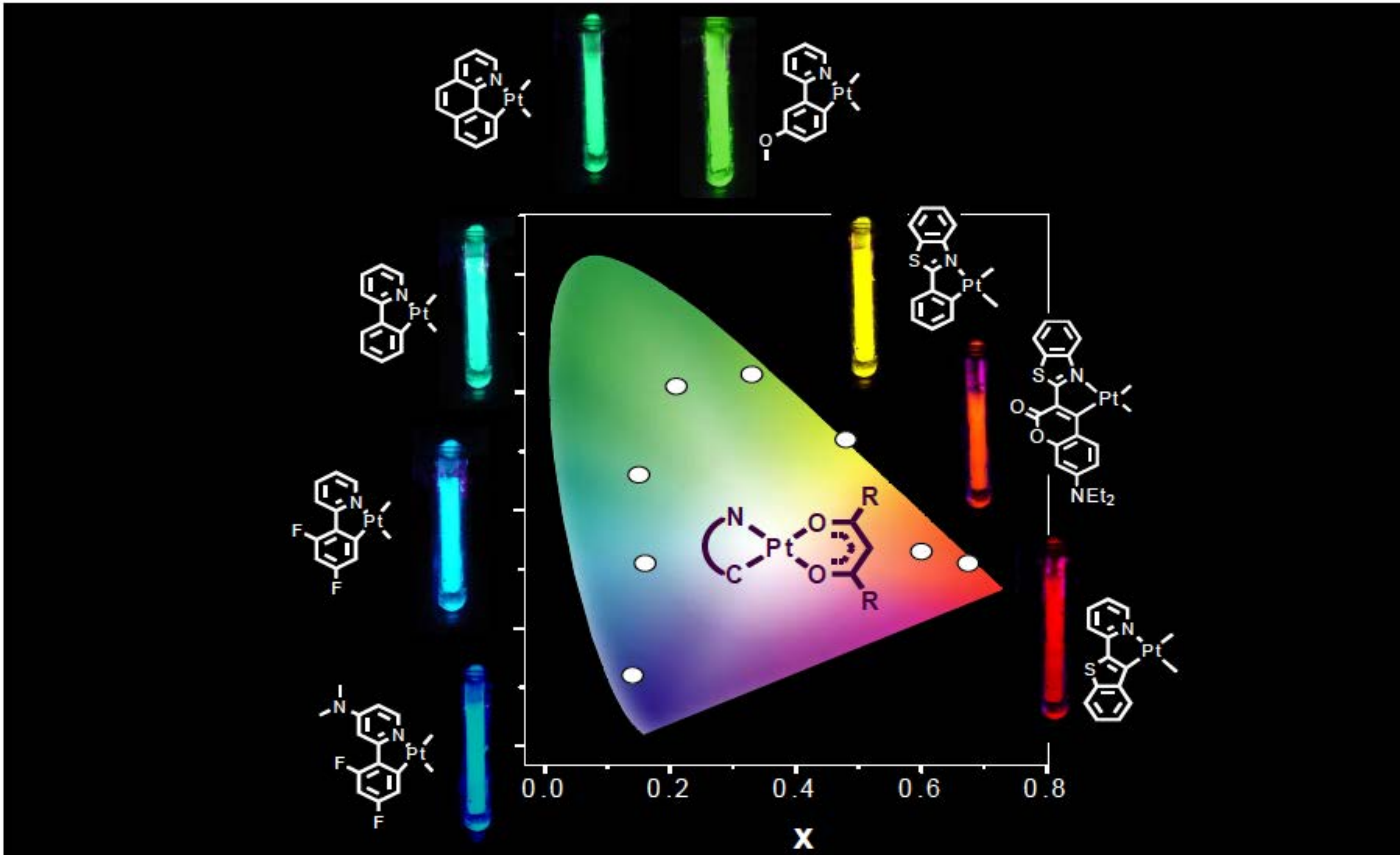


Efficient red EL emission from triplet excitons: $\eta_{ext} \sim 2.2\%$ @ 100 cd/m^2

M. A. Baldo, *et al*, Nature **395**, 151 (1998)

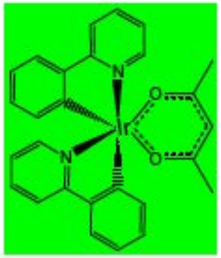
Cited 6450 times

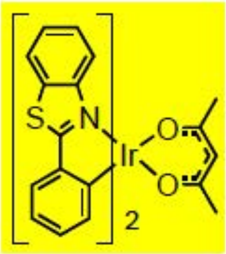
Platinum Complexes

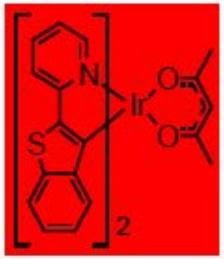


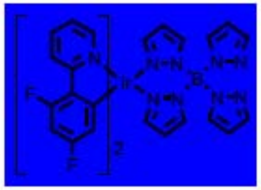
Brooks, J. et al., *Inorg. Chem.*, **2002**, *41*, 3055-3066

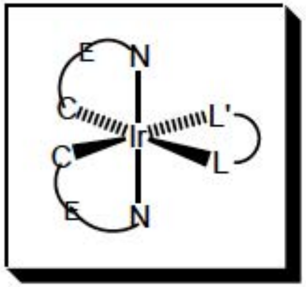
Iridium Complexes





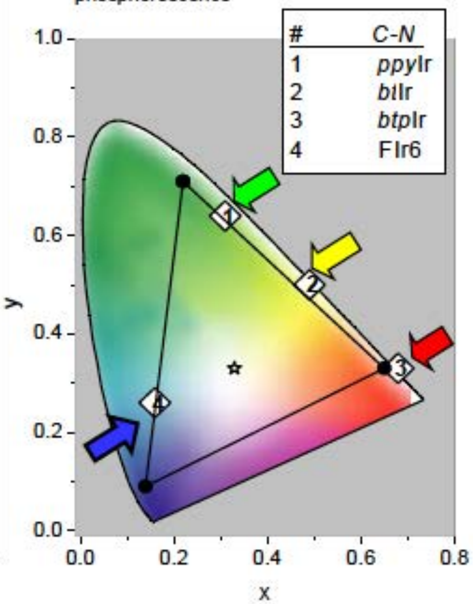






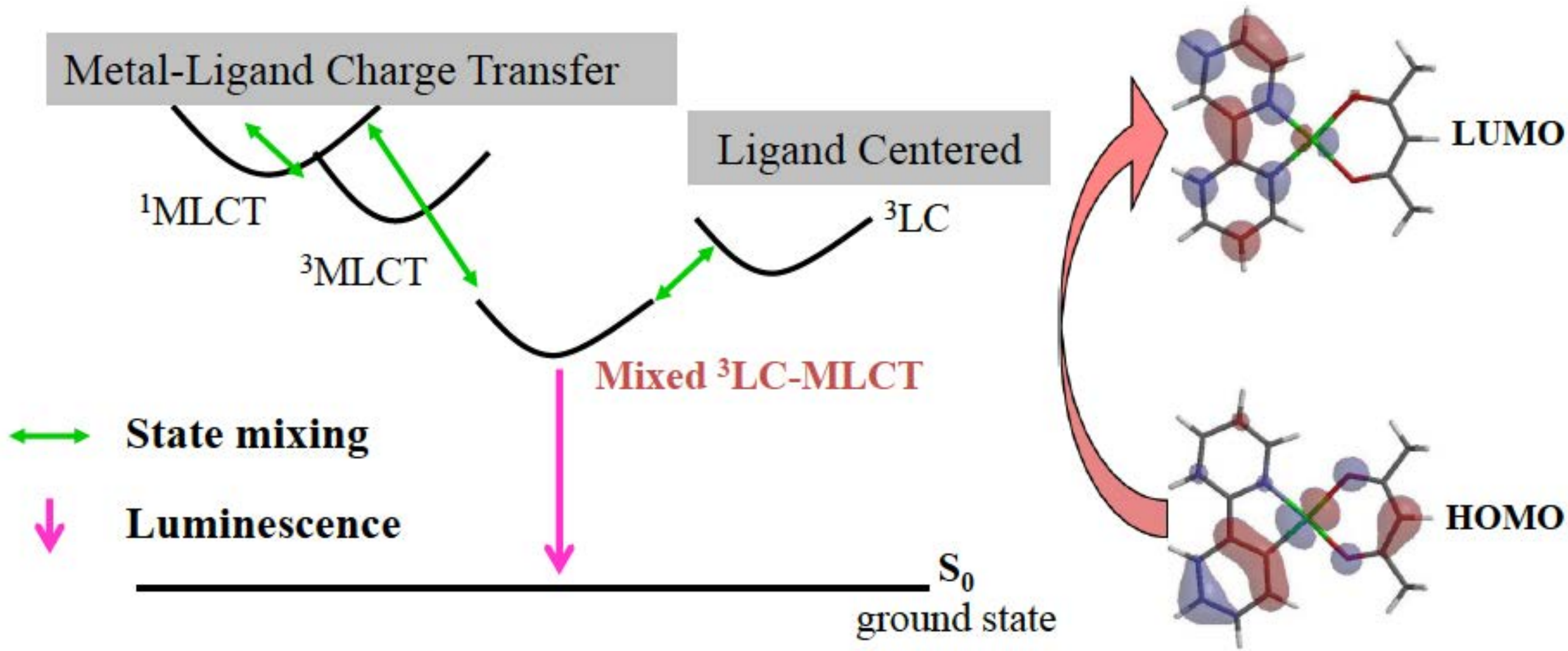
OLED Color	Max. QE, %	Max. Lm/W	Emitter	Reference
Green	**19**	**60**	***ppy*$_2$Ir(acac)**	Adachi *et al.*, *Appl.Phys.Lett.*(2001).
Yellow	**9.7**	**11**	***bt*$_2$Ir(acac)**	Lamansky et al., *JACS.* (2001).
Red	**7**	**5**	***btp*$_2$Ir(acac)**	Adachi *et al.*, *Appl.Phys.Lett.*(2001),
Blue	**11**	**13**	**FIr6**	Holmes *et al.*, *Appl.Phys.Lett.*(2003),

CIE coords. based on phosphorescence



Phosphorescent Emitter Material	Luminous Efficiency (Cd/A)	Operating Lifetime in hours (LT 95%)	Operating Lifetime in hours (LT 50%)
Deep Red	17	14,000	250,000
Red	30	50,000	900,000
Yellow	81	85,000	1,45,000
Green	85	18,000	400,000
Light Blue	50	700	20,000

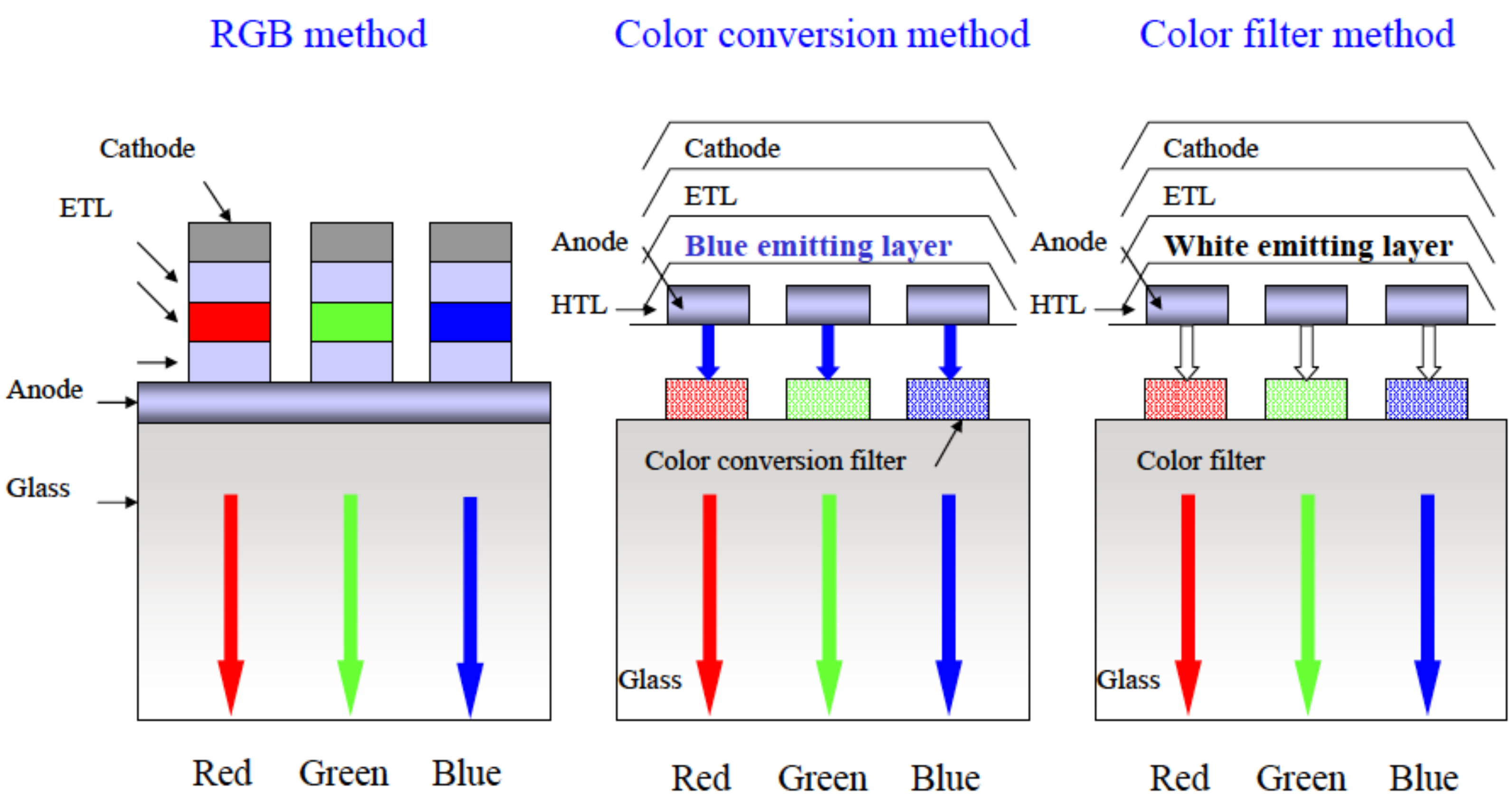
Color Tuning Mechanism



- Strong spin-orbit-coupling mixes singlet and triplet MLCT states, for M = Ir, Pt, Au, *etc*
- Mixing of 1MLCT and 3MLCT states with the 3LC state creates a hybrid 3(LC-MLCT) state with a largely allowed transition and a short triplet lifetime.
- p* is the LUMO (largely pyridyl), while the HOMO is phenyl/Pt based.
- **Color tuning of the emission can be achieved either by changing LC or MLCT.**

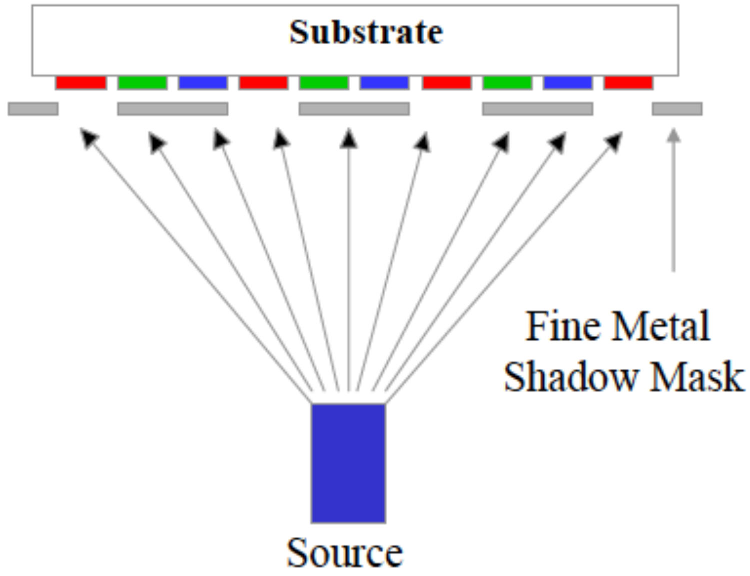
Fabrication of OLEDs

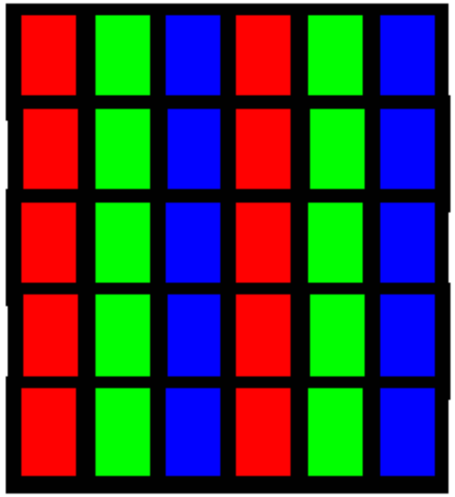
- Three Types:
  1. Vacuum Deposition/Vacuum Thermal Evaporation(VTE)
  2. Organic Vapor Phase Deposition
  3. Inkjet Printing



Vacuum Thermal Evaporation

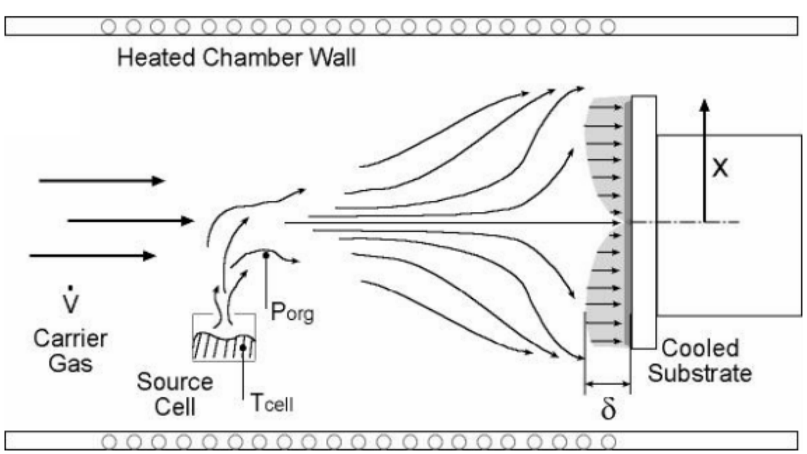
- Ideally in vacuum chamber
- Very low pressure (10^{-6} or 10^{-5} Torr)
- Molecules gently heated until evaporation
- Condensed as thin films on a cooled substrate
- Thickness of each layer can be precisely controlled
- Disadvantages
    - Evaporant condensed on cold walls can flake off, contaminating the system and substrate
    - Very difficult to control uniformity and doping concentration over large areas
    - Very expensive and inefficient





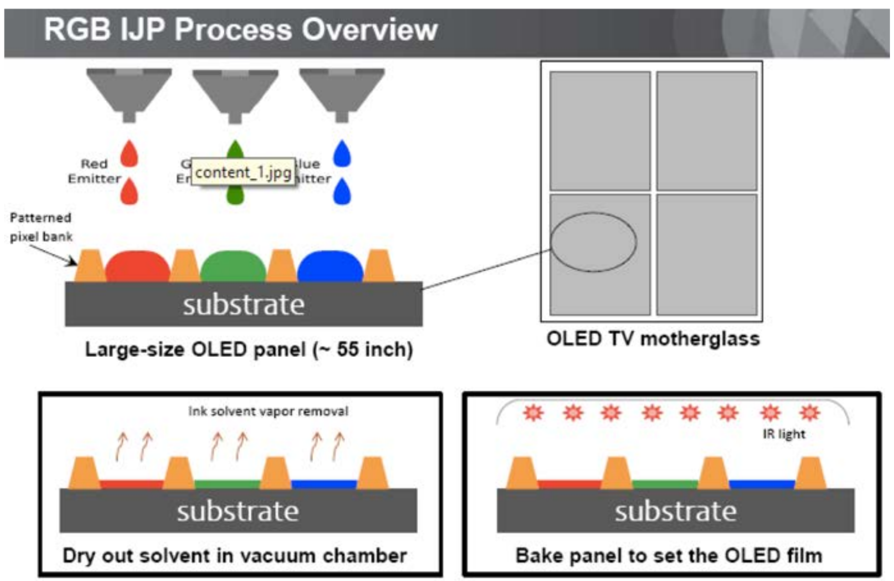
Organic Vapor Phase Deposition

- Process
  - Under low-pressure and in a hot-walled reactor chamber
  - Carrier gas transports evaporated organic molecules onto cooled substrates
  - Condensed into thin films
- Improves control over doping
  - Controlled by both temperature and carrier gas flow rate
- Better for large-area substrates
- Advantage
  - Use of a carrier gas increases the efficiency
  - Reduces cost

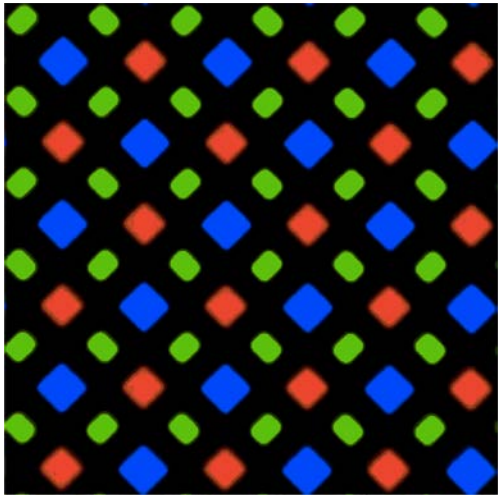


Inkjet Printing

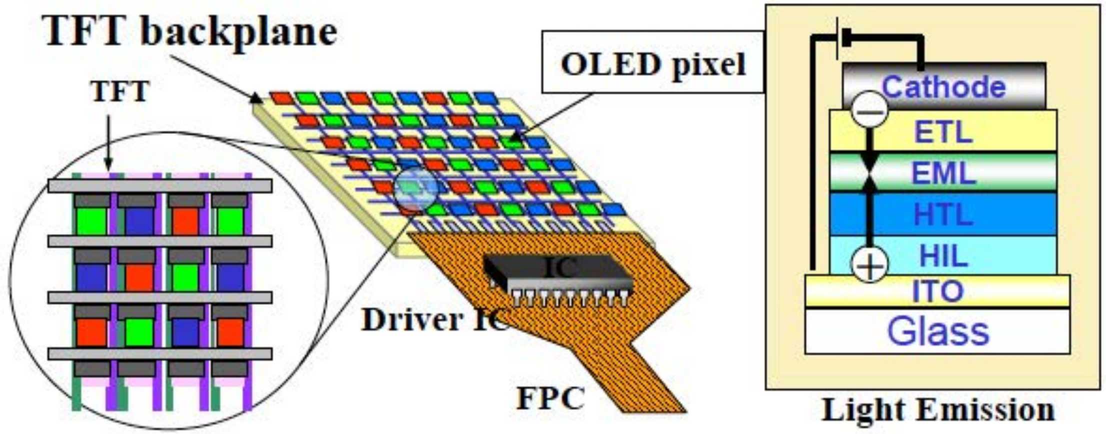
- Process
  - Organic materials diluted into a liquid and sprayed onto substrates
    - Similar to a standard inkjet printer
- Organic Vapor Jet Printing
  - Developed at Princeton
  - Uses vaporized organics instead of the liquid based jets of other inkjet printers
- Current Equipment Manufacturer
  - MIT spinout Kateeva
- Advantages
  - Drastically reduces manufacturing costs
  - Allows OLEDs to be printed onto very large films
    - Examples - 80 inch TV screen or electronic billboard

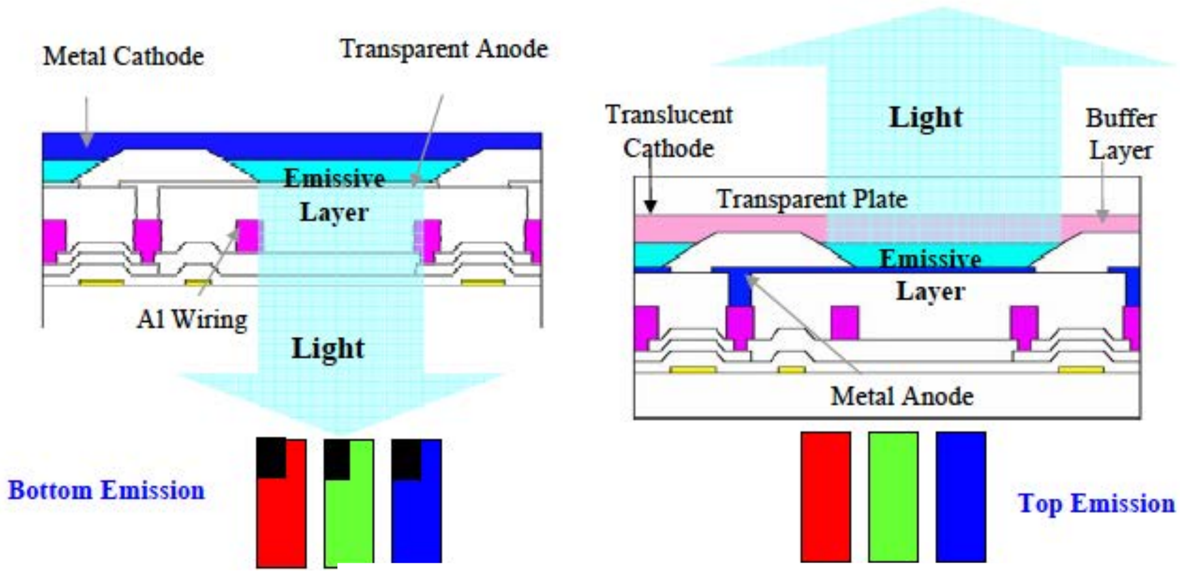


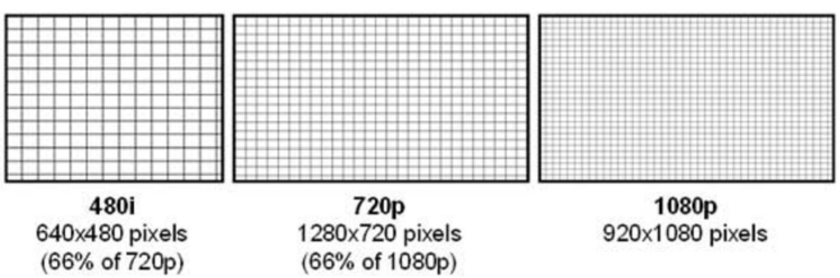
AMOLED

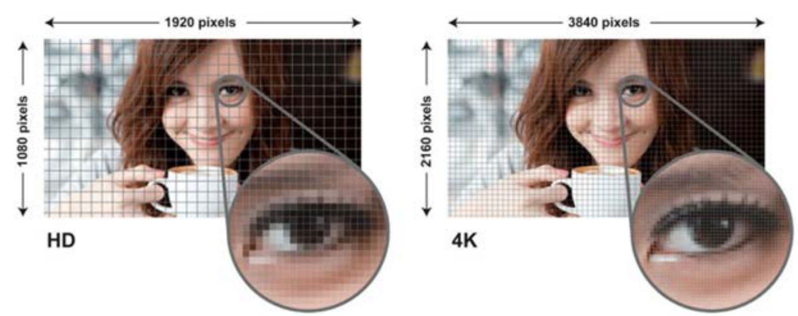


iPhone X Diamond Sub-Pixels

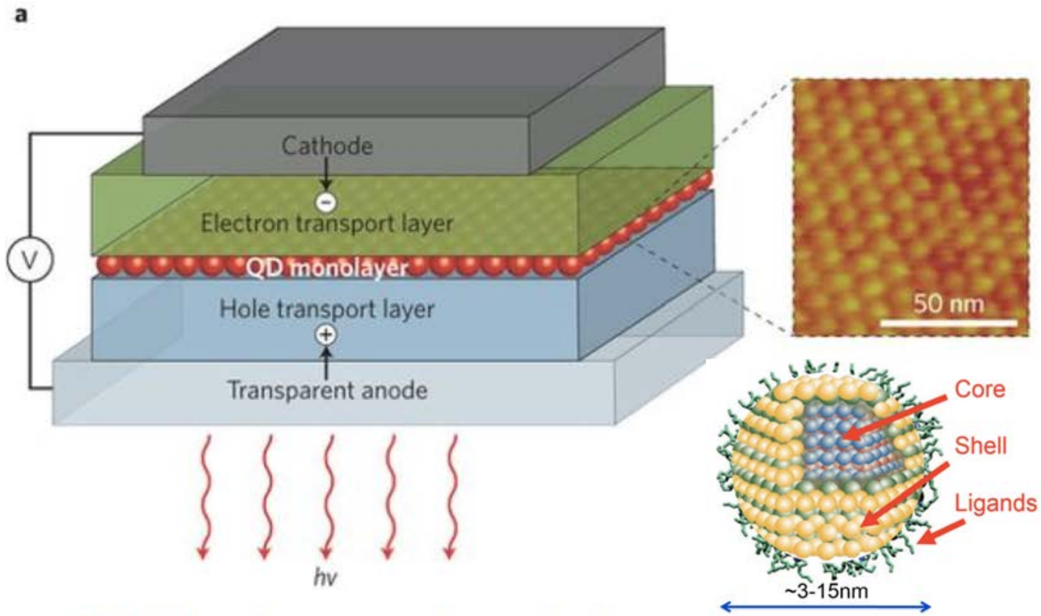


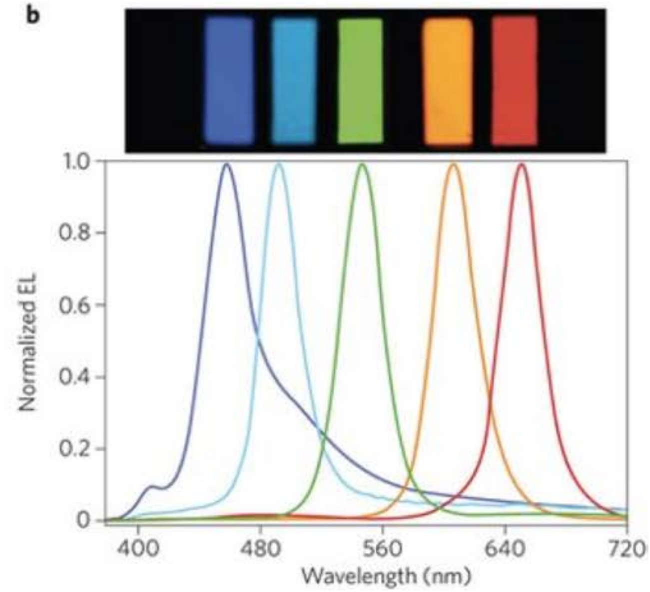






Electrically Driven Quantum Dot LEDs



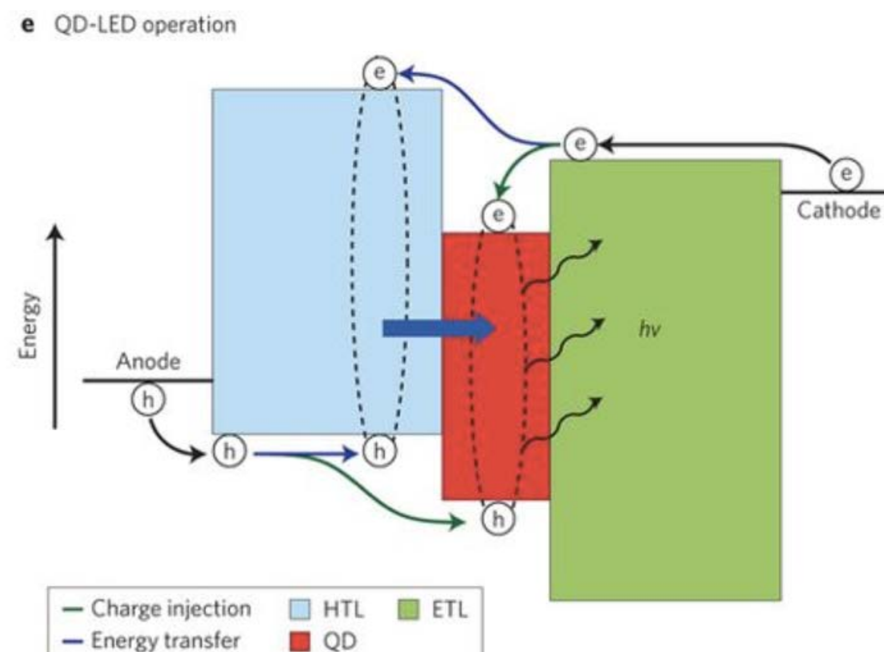


Electroluminescence from single monolayers of nanocrystals in molecular organic devices

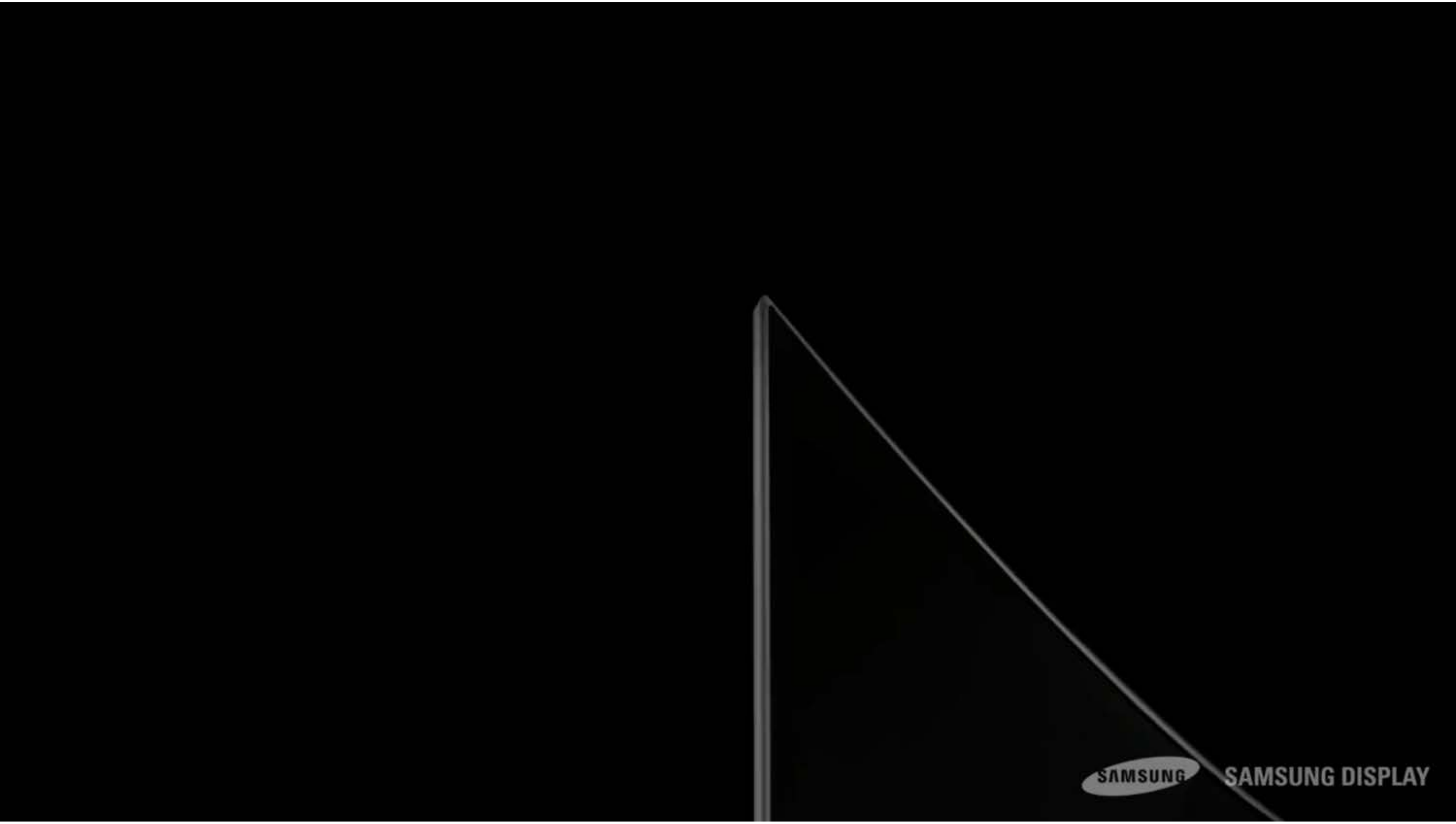
Seth Coe*†, Wing-Keung Woo†‡, Moungi Bawendi‡ & Vladimir Bulović*

* *Laboratory of Organic Optoelectronics, Department of Electrical Engineering and Computer Science,*
‡ *Center for Materials Science and Engineering, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*
† *These authors contributed equally to this work*

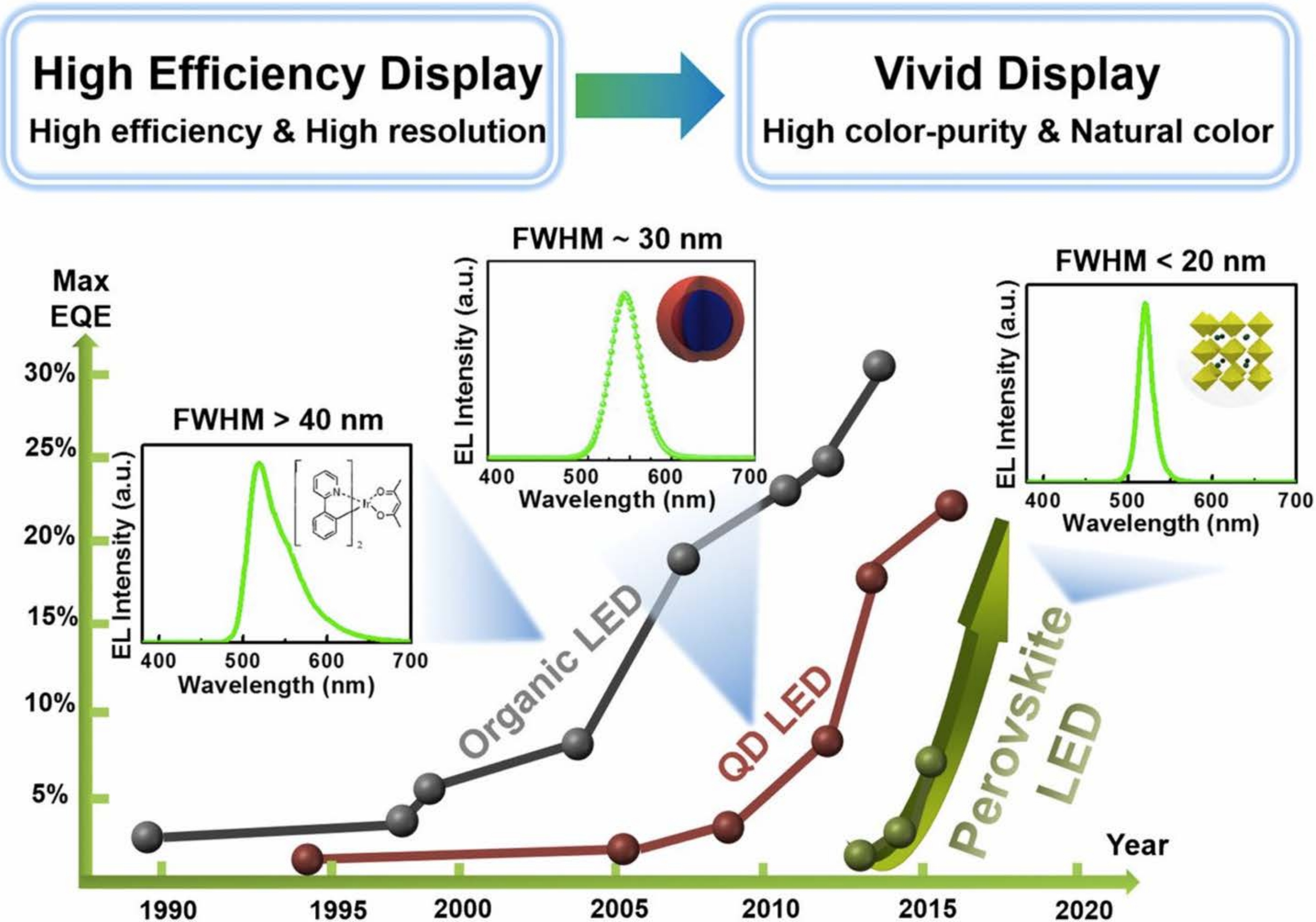
The integration of organic and inorganic materials at the nanometre scale into hybrid optoelectronic structures enables active devices[1–3] that combine the diversity of organic materials with the high-performance electronic and optical properties of inorganic nanocrystals[4]. The optimization of such hybrid devices ultimately depends upon the precise positioning of the functionally distinct materials. Previous studies[5,6] have already emphasized that this is a challenge, owing to the lack of well-developed nanometre-scale fabrication techniques. Here we demonstrate a hybrid light-emitting diode (LED) that combines the ease of processability of organic materials with the narrow-band, efficient luminescence of colloidal quantum dots[7] (QDs). To isolate



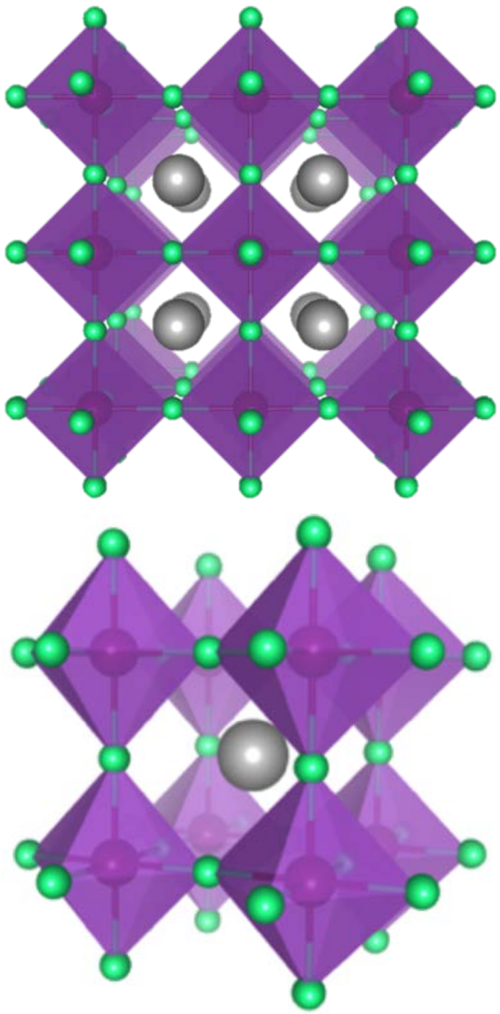
Quantum Dot LEDs



Perovskite LEDs



Metal Halide Perovskites



ABX_3

A = Cs, CH_3NH_3
B = Pb, Sn, etc.
X = Cl, Br, I

Attractive Features:

- Earth abundant elements
- Solution processable
- Low temperature processing
- Excellent optical properties
- Excellent electronic properties
- High structure tunablity

The First Report of Efficient Perovskite LEDs at R.T.

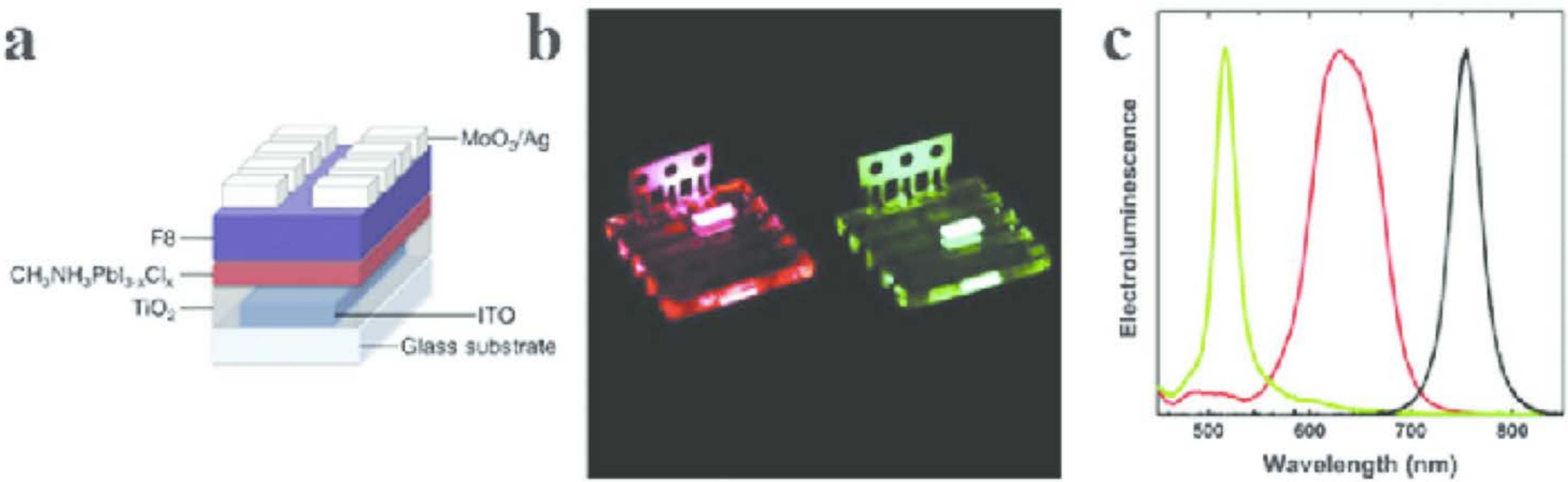
nature nanotechnology

LETTERS

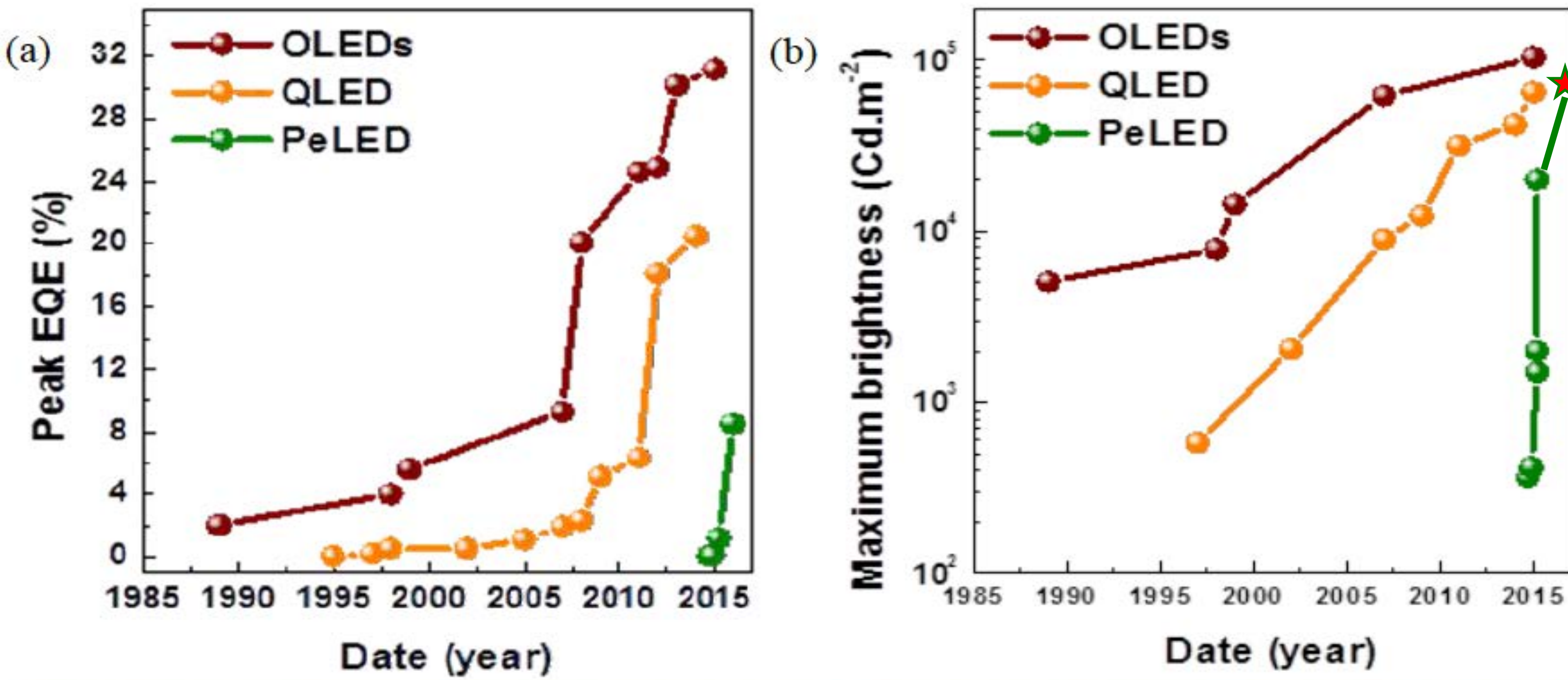
PUBLISHED ONLINE: 3 AUGUST 2014 | DOI: 10.1038/NNANO.2014.149

Bright light-emitting diodes based on organometal halide perovskite

Zhi-Kuang Tan[1], Reza Saberi Moghaddam[1], May Ling Lai[1], Pablo Docampo[2], Ruben Higler[1], Felix Deschler[1], Michael Price[1], Aditya Sadhanala[1], Luis M. Pazos[1], Dan Credgington[1], Fabian Hanusch[2], Thomas Bein[2], Henry J. Snaith[3] and Richard H. Friend[1]*



The State of The Art



Phosphorescent Emitter Material	Luminous Efficiency (Cd/A)	Operating Lifetime in hours (LT 95%)	Operating Lifetime in hours (LT 50%)
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Yellow	81	85,000	1,45,000
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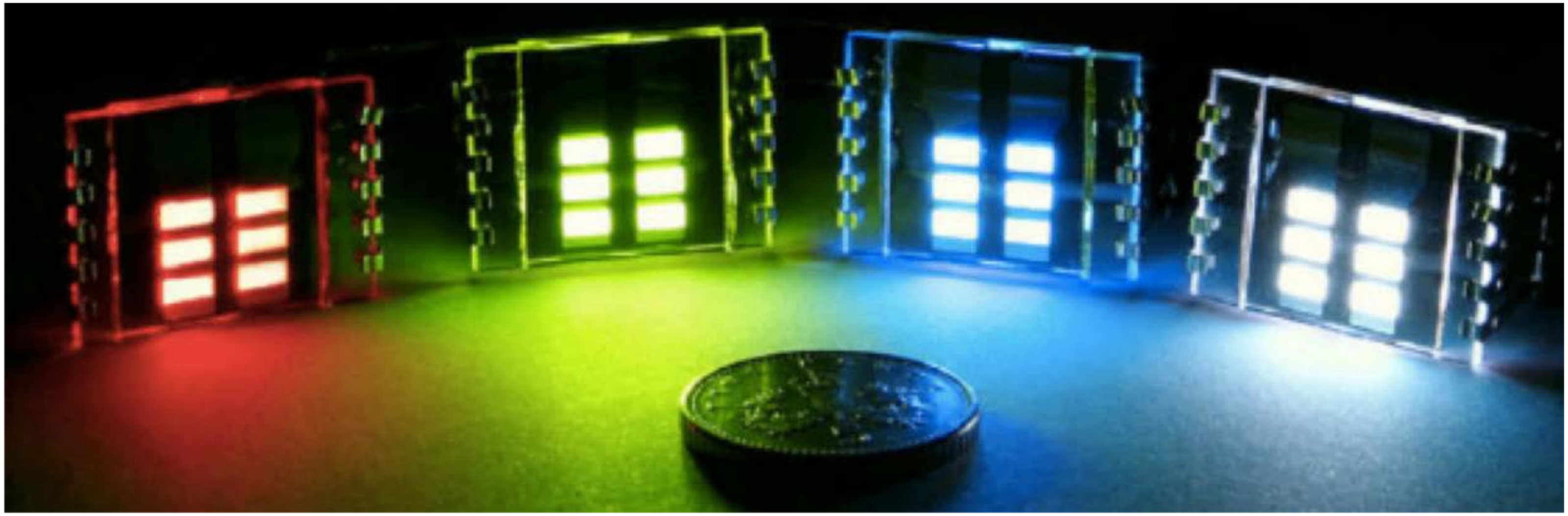
Light Blue	50	700	20,000

Outlooks and Challenges



- **Efficiency** (Approaching that of OLEDs)?
- **Full color display and solid state lighting** (Color tuning)?
- **Stability** (Material and device degradations)?
- **Cost-effectiveness** (Material and processing costs)?
- **Environmental concerns** (Lead free)?