White Organic Light Emitting Diodes for Super-thin Flat Panel Lighting

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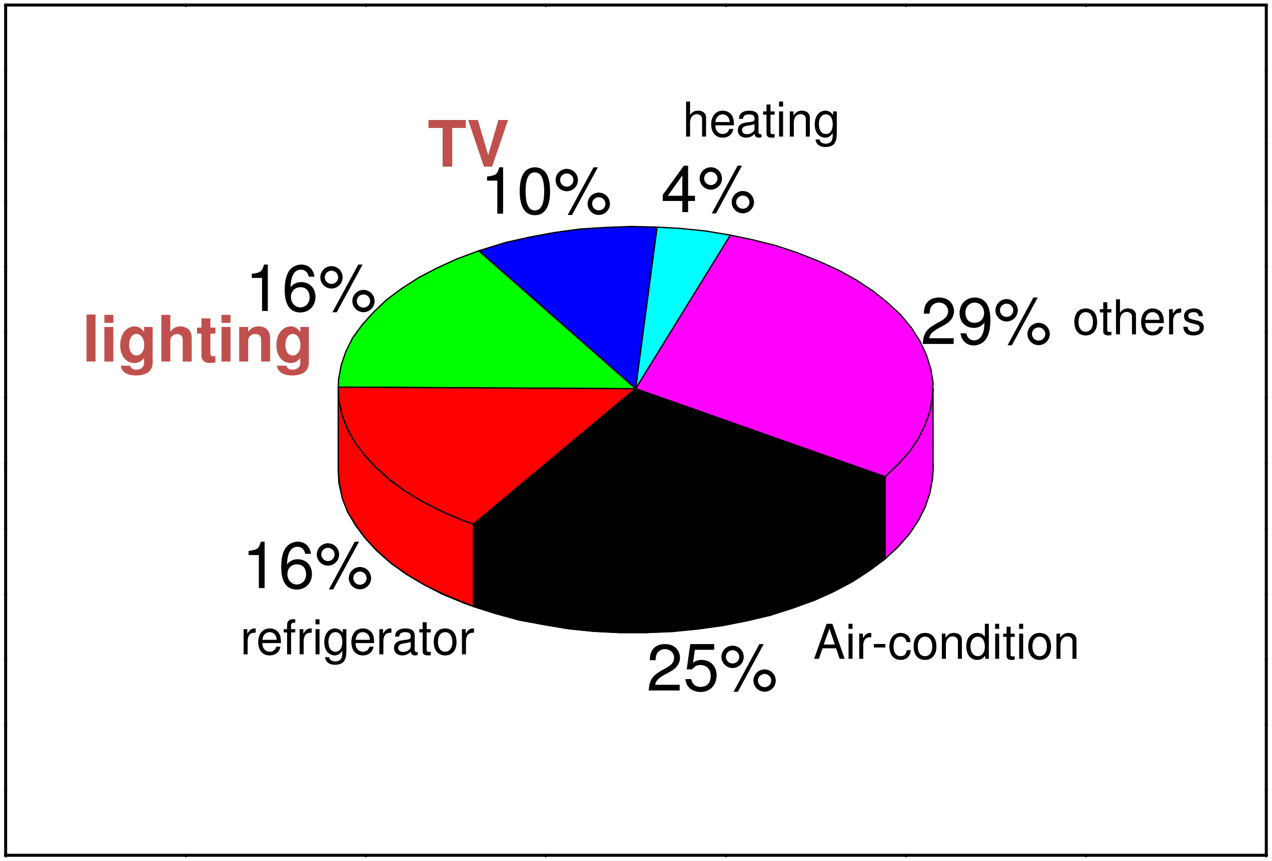
Outline

1.Why white OLED is necessary for lighting ?

2. What is OLED ?

3. How to make white OLEDs ?

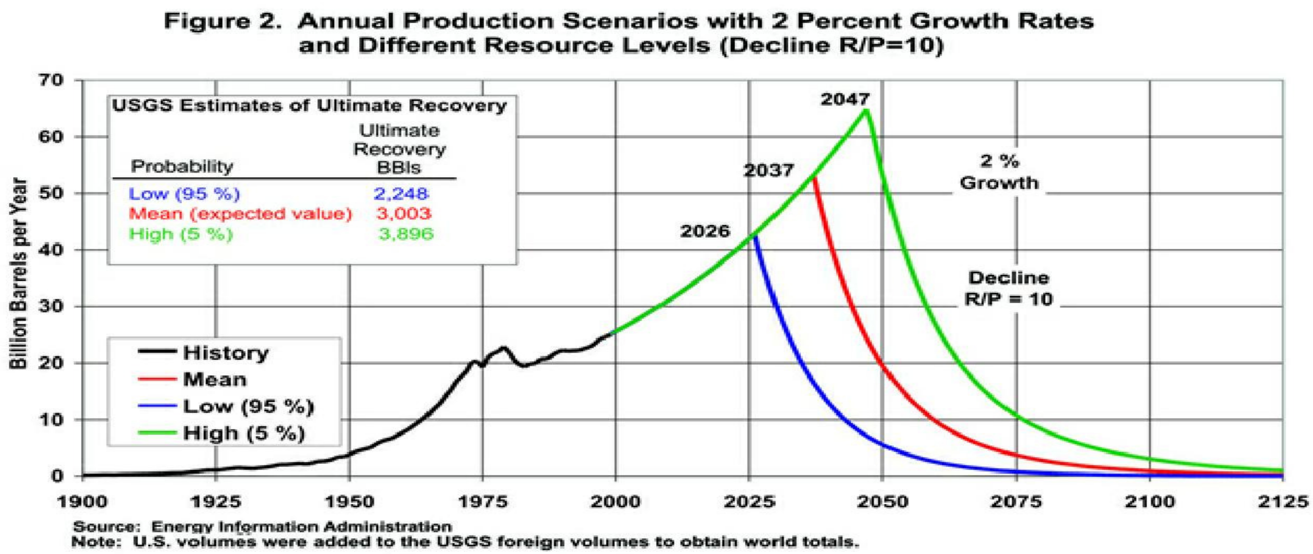
FNMA09 L'Aquila-Sulmona, September 28, 2009 electricity consumption in Japanese houses



Japanese Government report

Why OLED lighting and OLED displays are needed ?
Because of **Shortage of Oil Resource**

Production of Oil



Long-Term World Oil Supply Scenarios:The Future Is Neither as Bleak or Rosy as Some Assert
By John H. Wood, Gary R. Long, David F. Morehouse
Posted: August 18, 2004
http://www.eia.doe.gov/pub/oil_gas/petroleum/feature_articles/2004/worldoilsupply/oilsupply04.html

とんがり帽子型のピークを想定した場合には、ターニングポイント
(ピーク時)に必要なクサビは恐るべき量になる＝持続可能ではない

No more oil after 40 years ?

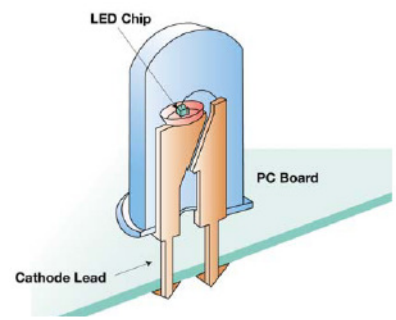
Low-energy consuming lighting and display are needed.

Power efficiency of lighting

power efficiency: $\eta = \pi L(cd)/J(A)V(V)$

Incandescent lamp(100W) : 16～18 lm/W
Xe lamp : 25～35 lm/W

Fluorescent lamp: 40～110 lm/W



White LED (Cree, USA) : 131 lm/W
White LED (Nichia, Japan) : 150 lm/W

White OLED (Universal Display Corp., USA) : 102 lm/W (2008.6.) at1000cd/m^2
White OLED (Novaled AG, Germany) : 90 lm/W at 1000cd/m2 ,
with attachment 124 lm/W (2009.5.)

Problems:

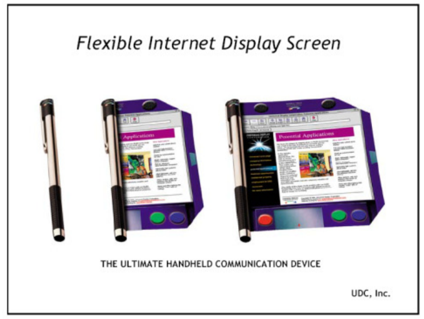
LED: shortage of rare metals like In and Ga
Fluorescent lamp : containing Hg

Organic Electronics

Everything by organic materials

Displays

Electronic paper →

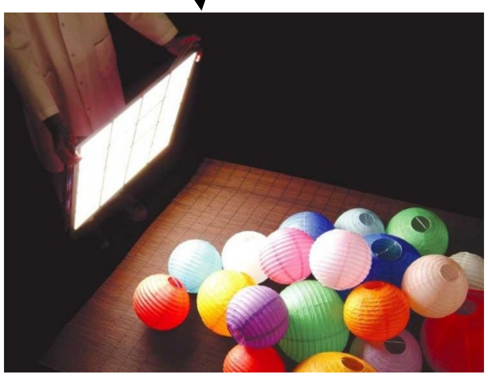


Transistor, Condenser

Solar cell

Lasers : Easily tunable and any emitting color

New Lighting using white OLED

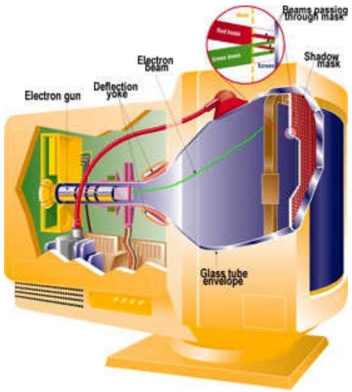


General Electric Global Research Co.

Fraunhofer Institut für Photonische Mikrosysteme (IPMS) in Dresden

OSRAM

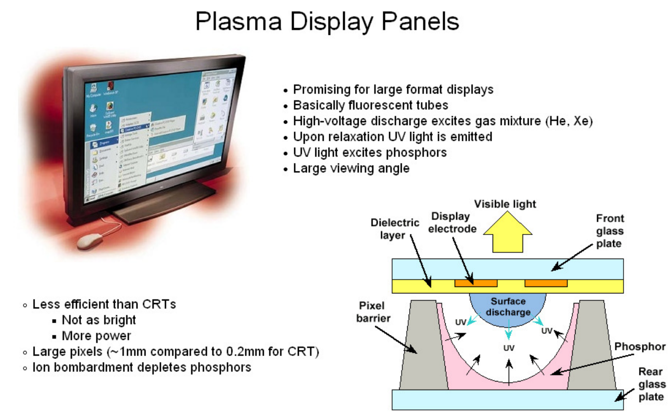
Progress of TV displays



CRT-TV

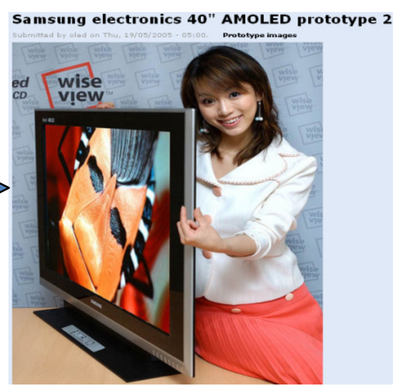
Liquid Crystal Display

Contrast: 3,000 : 1



Plasma Display Panel

Contrast: 8,000 : 1

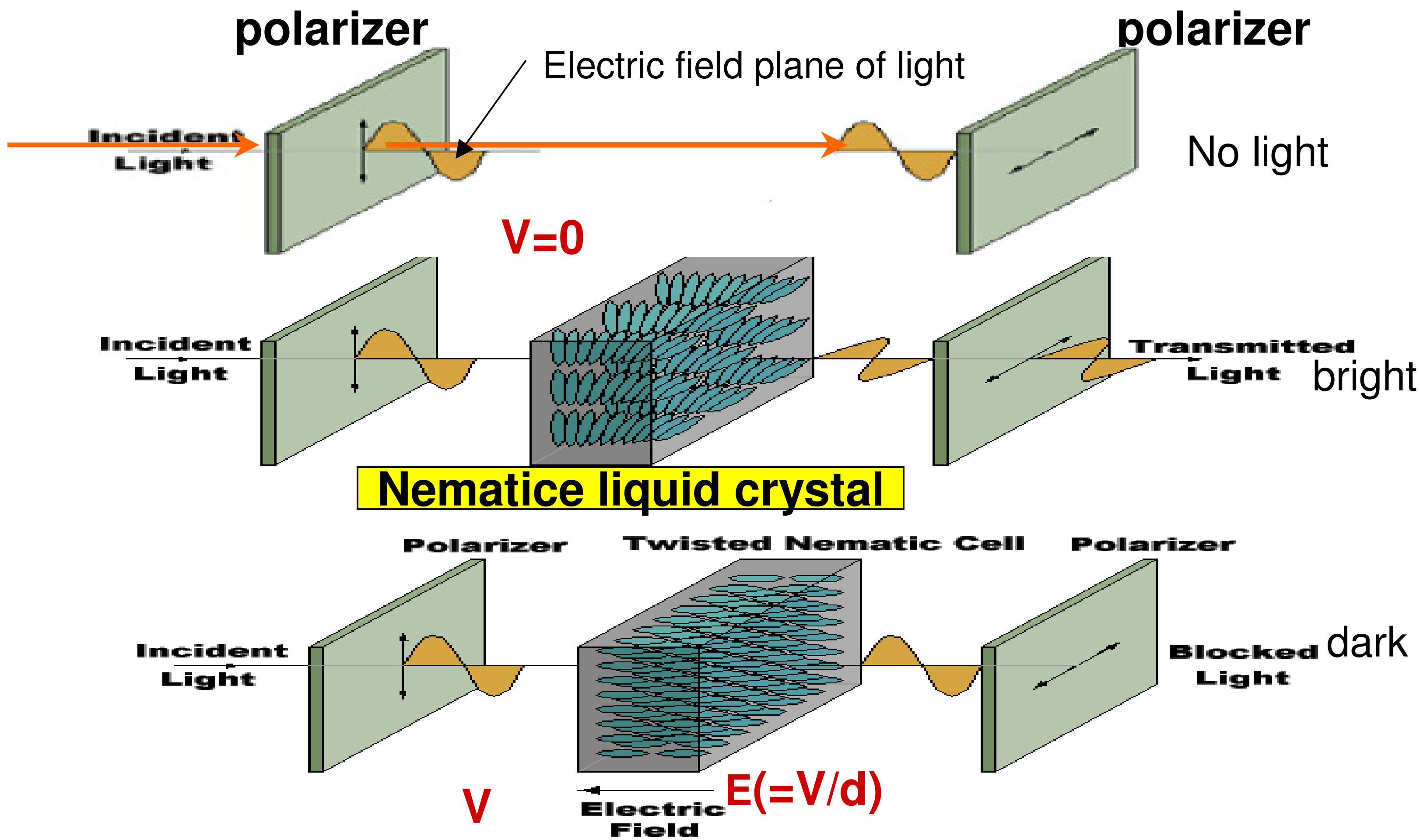


Organic Light emitting diode (OLED) display

SONY OLED 11’ TV「XEL-1」
Dec., 2007

Thickness: 3 mm
Consumption power: 45 V
Contrast: 1,000,000:1

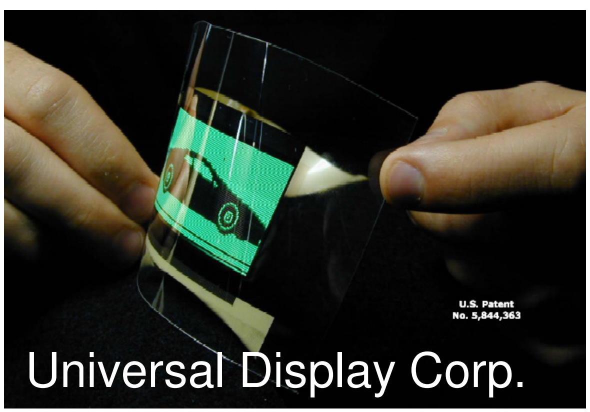
Principle of LC Display



Orientation of LC is changed by applied voltage

Advantage of OLED devices

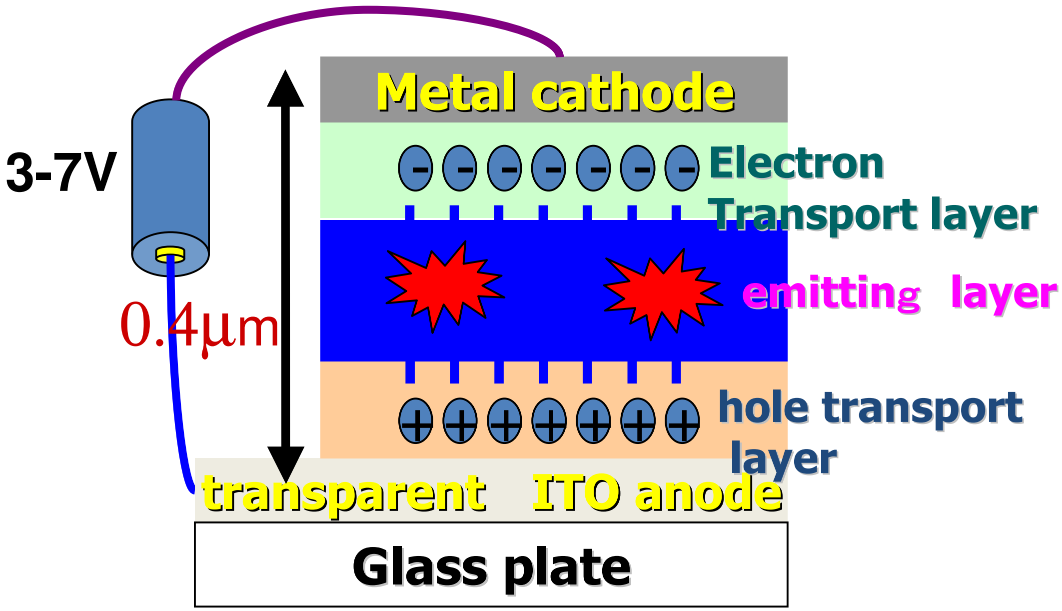
1. Self-emission, No back-light
2. High response, wide viewing angle
3. High contrast image
4. Super-thin flat, lightweight
5. Flexible, paper-like display
6. Low voltage operation 5V: Low cost operation
7. Organic materials: Easy manufacturing
8. Low cost for production



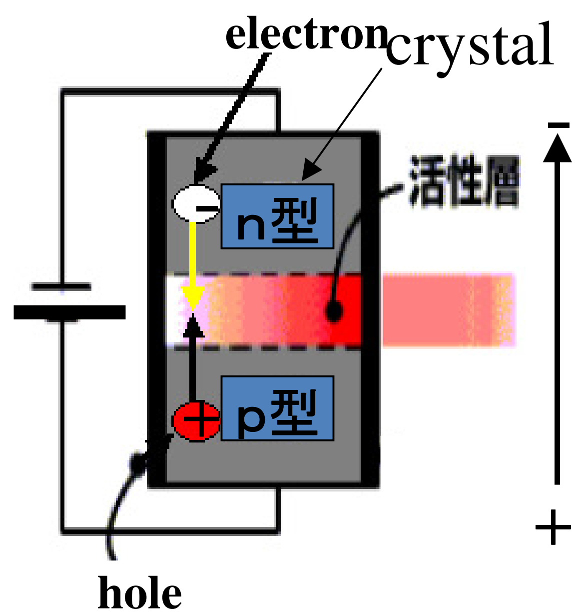
Fraunhofer Institut für Photonische Mikrosysteme (IPMS) in Dresden

OSRAM

Organic Light Emitting Diode (OLED) with organic semiconductors



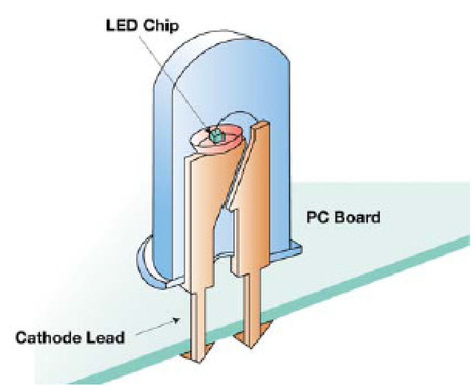
Inorganic LED



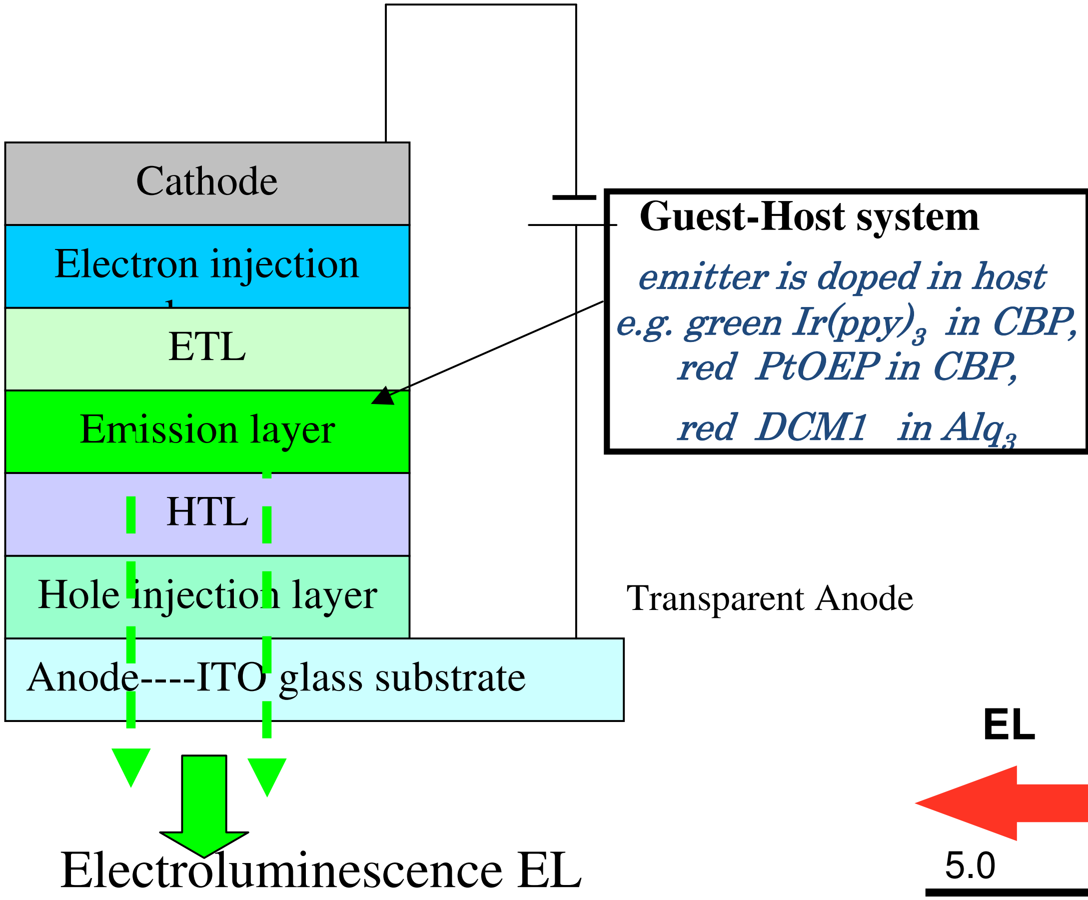
Emission by Recombination of electron and hole : Electroluminescence

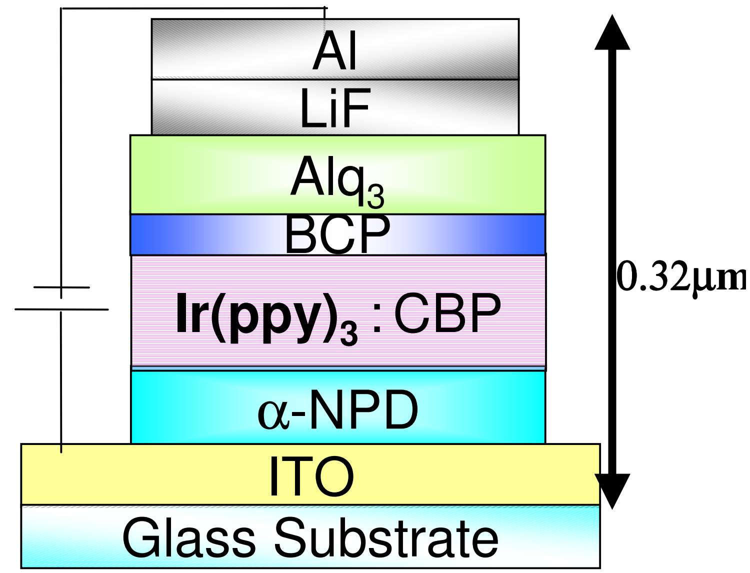
Green and Red OLEDs

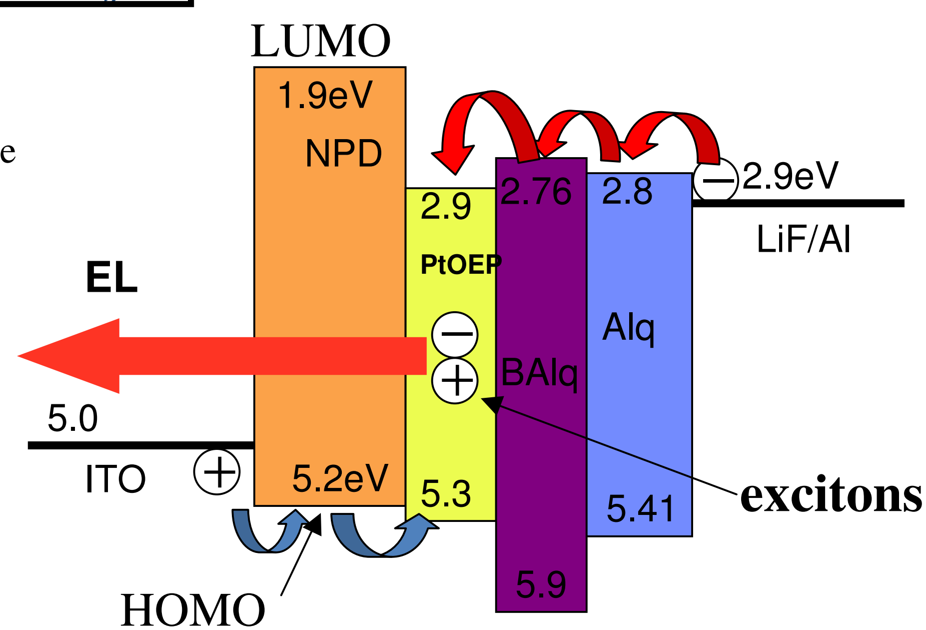
White OLEDs



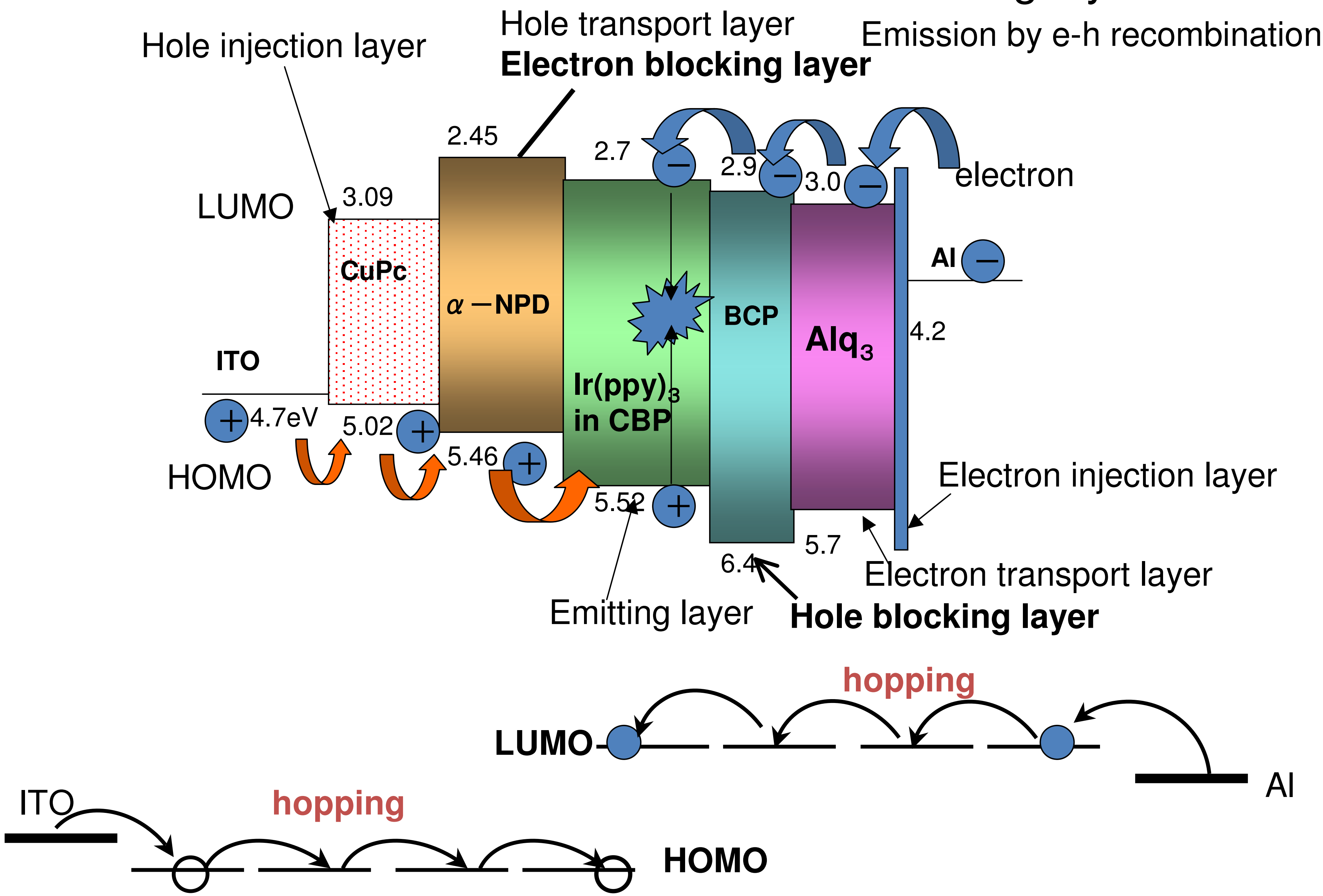
Actual OLED with multi-layers for carrier balance and confinement to make high density excitons



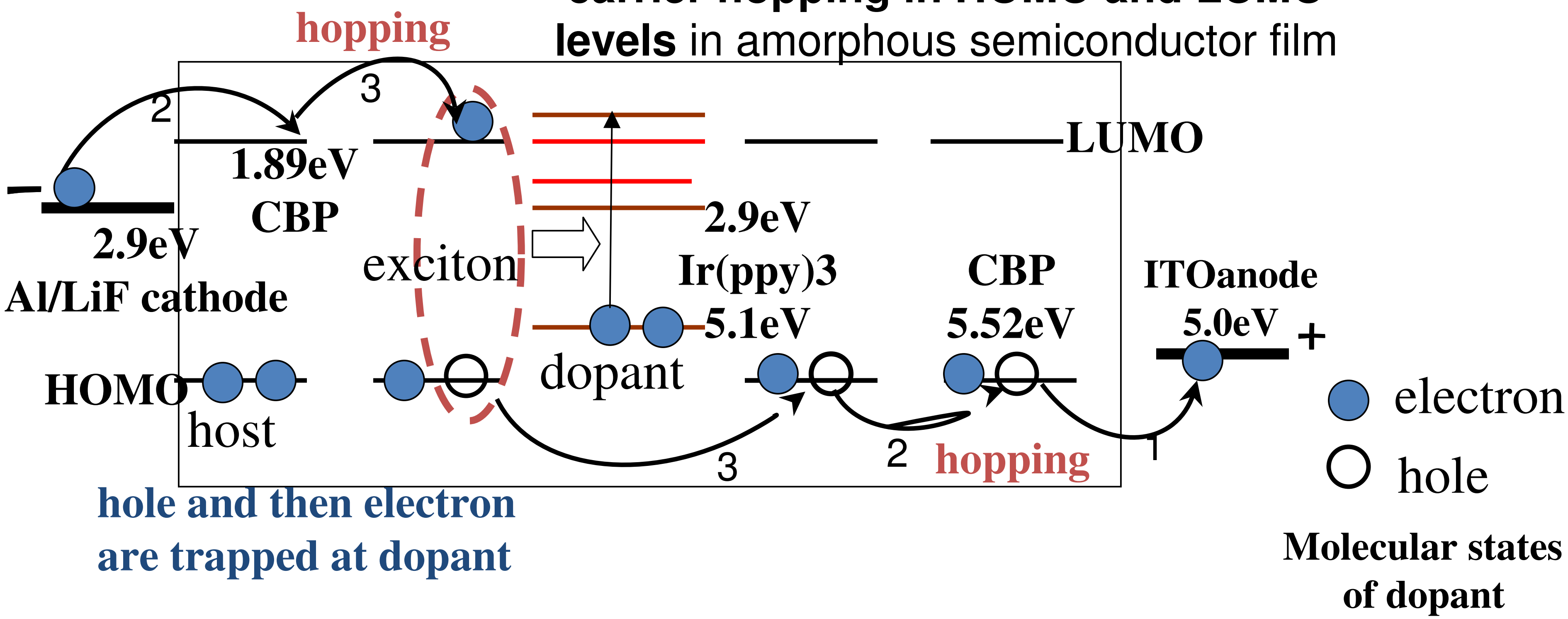




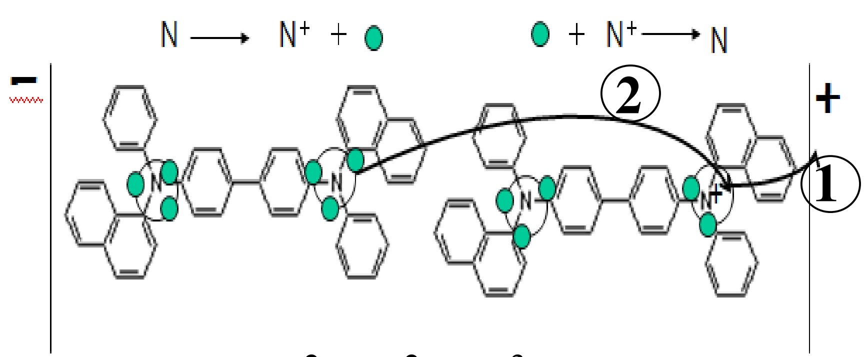
confinement electrons and holes in emitting layer



carrier hopping in HOMO and LUMO levels in amorphous semiconductor film



Removal of electron from hole transport molecules α －NPD



N：$(1s)^2(2s)^2(2p)^3$

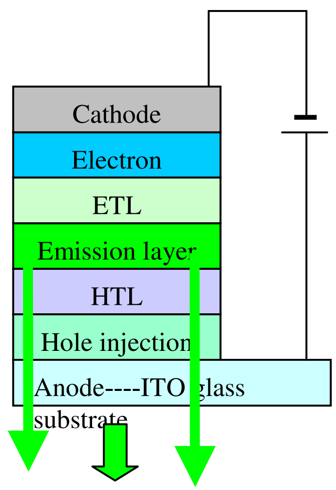
How to increase the quantum efficiency in OLED ?

1. **High numbers of injected electrons and holes in emitting layer**
   good injection layer
   high carrier mobility materials
   confinement of electrons and holes

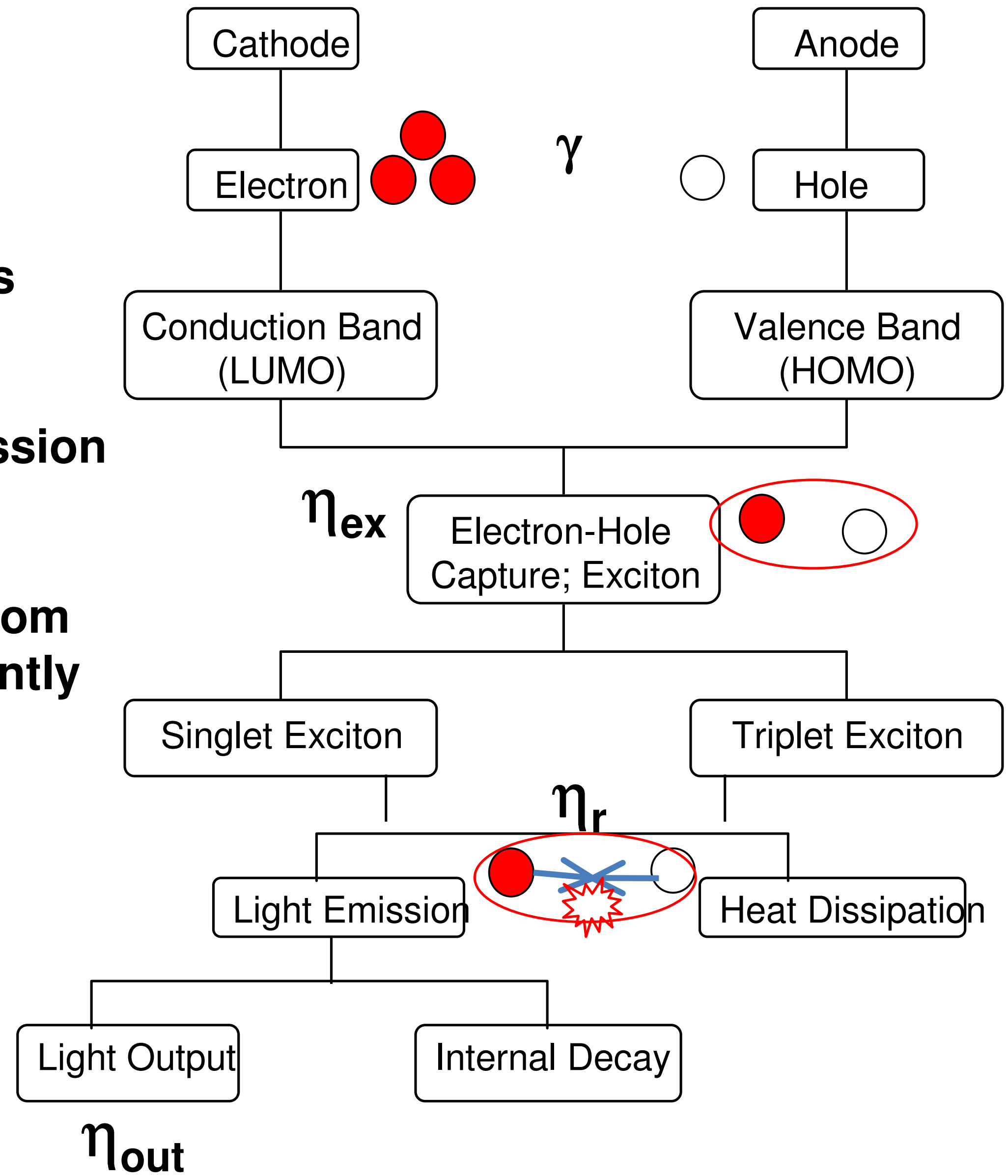
2. **Same number of electrons and holes**
   because exciton is formed by e+h

3. **All excitons should be used for emission**
   Phosphorescent emitter is the best.

4. **Emission should be taken outside from emitting layer inside of OLED efficiently**

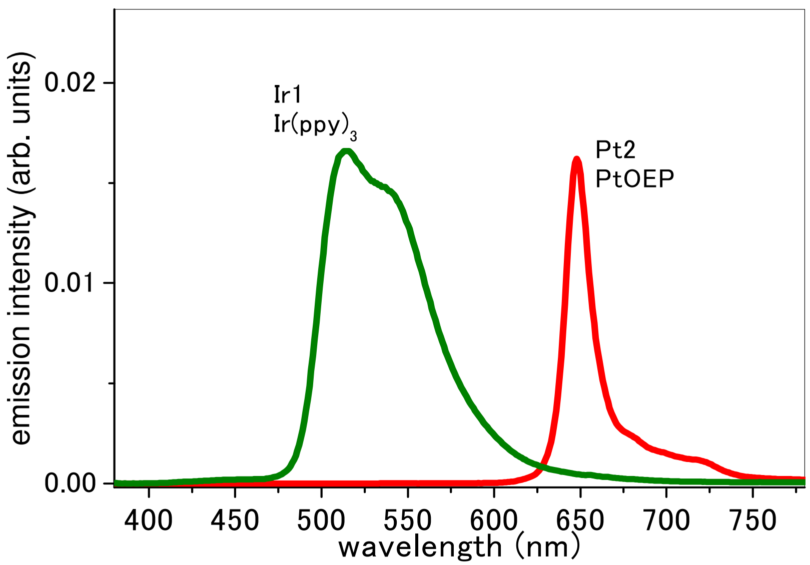


Scheme of EL Process

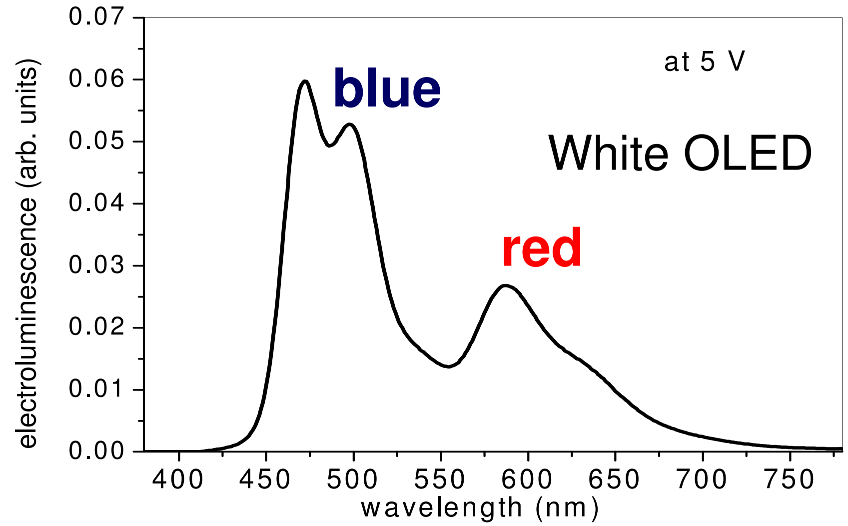


Electroluminescence spectra

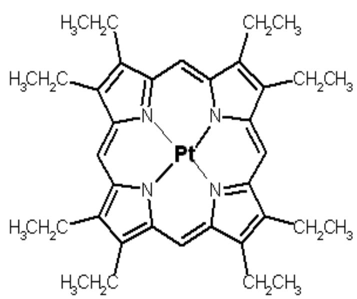
Mono color

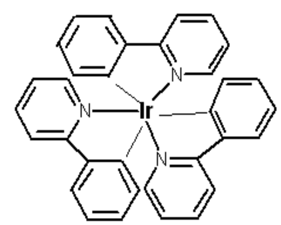


white color



PtOEP (Platinum octaethylporphyrin)





$Ir(ppy)_3$

tris(2-phenylpyridine) iridium

Currently available OLED displays

Cellar phone with OLEDs

Fujitsu

F900i

「FOMA F900ｉ」

F506i

「ムーバ® F506ｉ」

Feb., 2004 May, 2004

Main LCD 262,144 colors 2.4"TFT

Front OLED 4,096 colors 1.1"

ムーバ F506i

Kodak Digital Camera

LS433 LCD LS633 OLED

SAMSUNG AMOLED TL320 Digital camera

12.2 Mega Pixels

Kodak One-Seg OLED TV

Currently used OLED display

Victor Co. Audio compo

Pioneer Co., Display panel for automobiles

portable audio player

Matsushita Co.,

Sony

Olympus

What lighting is good for us ?

Materials should be seen under lighting just as seen under sun.

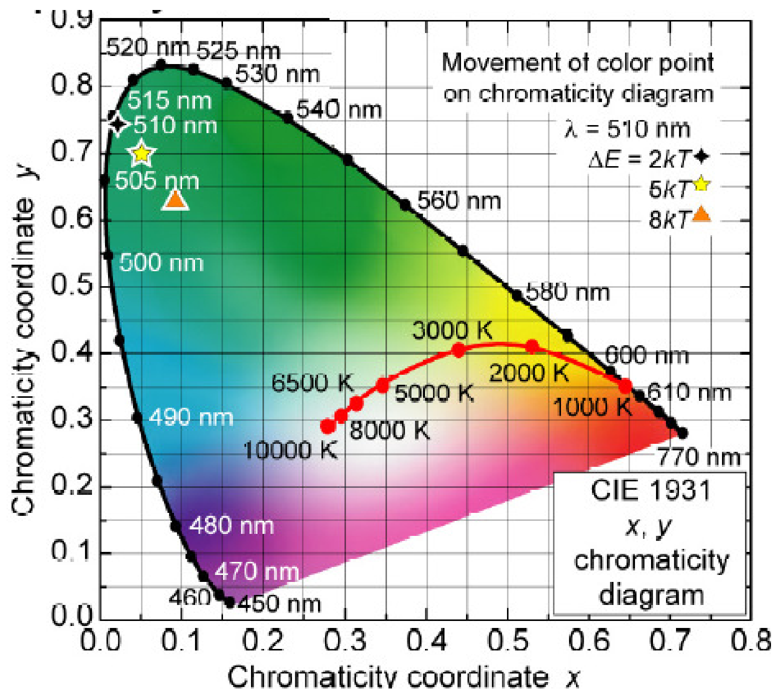
White light as sunshine

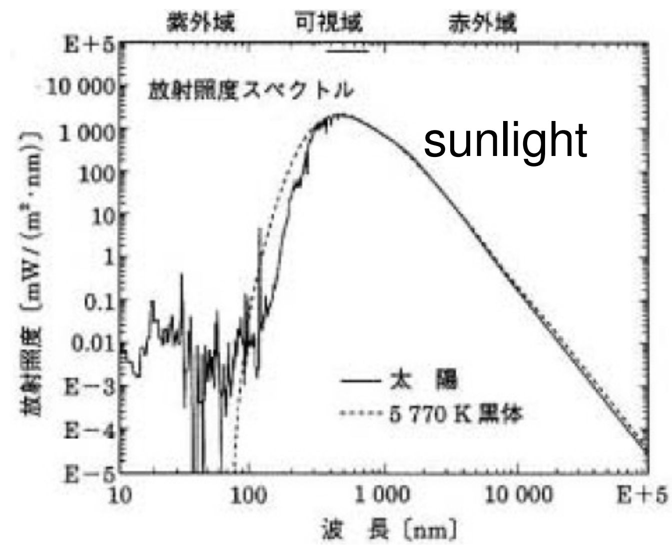
CRI color rendering index under sunshine CRI=100 (standard)

usual f. lamp **CRI 60**

3-λ f. lmap **CRI 80**

3-λ naturalf. lmap **CRI 90**





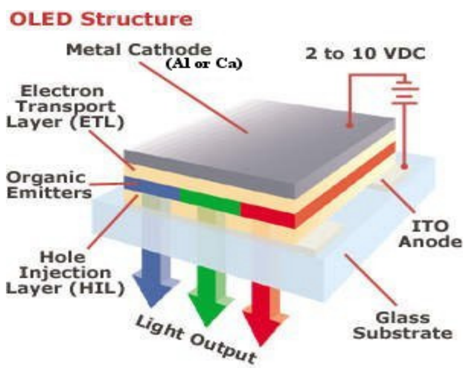
color temperature: 2500-6000K

chromaticity index CIE (0.33, 0.33)

CRI＞80

http://map.answerbox.net/landmark-368647-bbs-2.htm

generation of white light

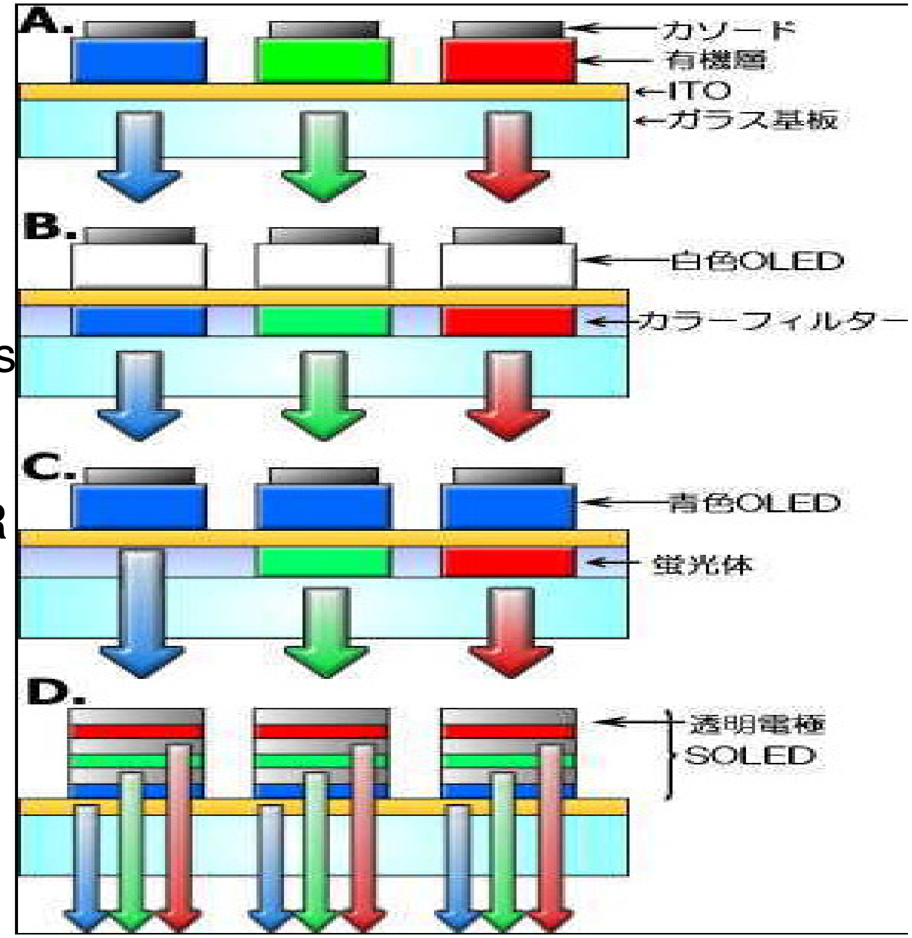


A. RBG parallel

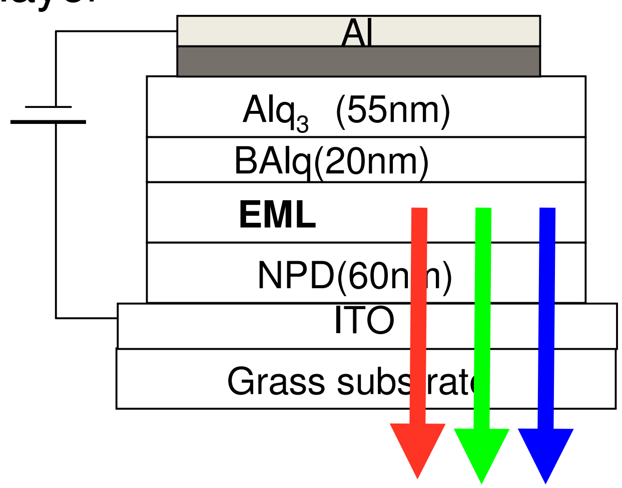
B. White with RGB color filters

C.Color conversion: B to G, B to R

D. Tandem structure

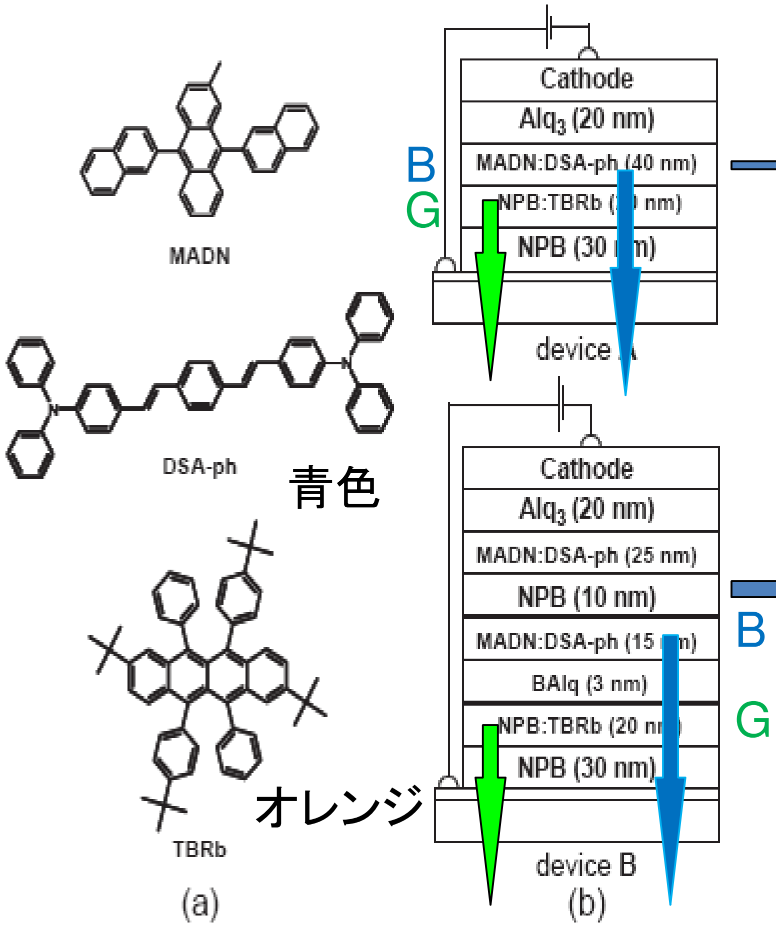


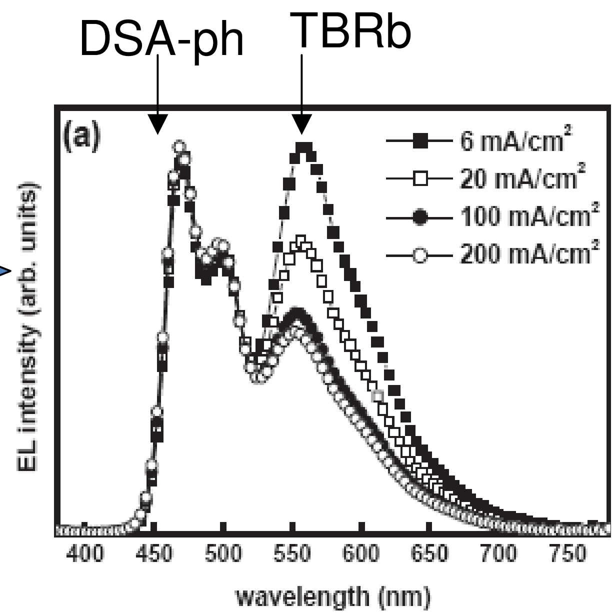
E. Single emitting layer

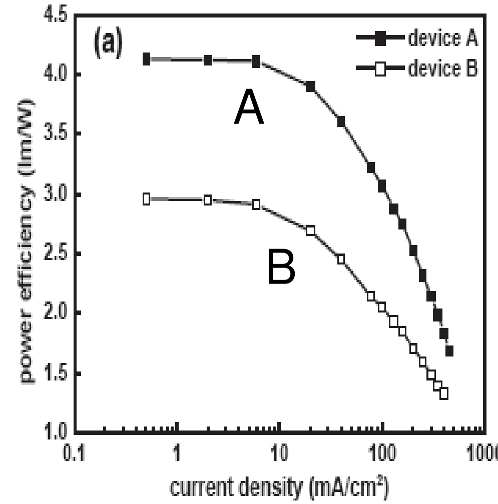


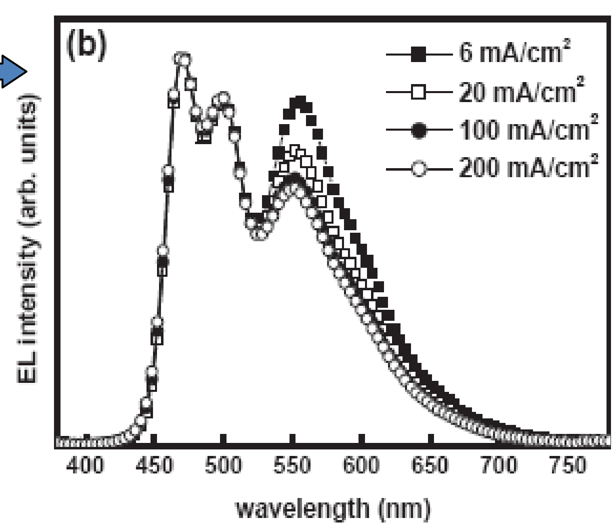
R,B emission
R,G,B emission

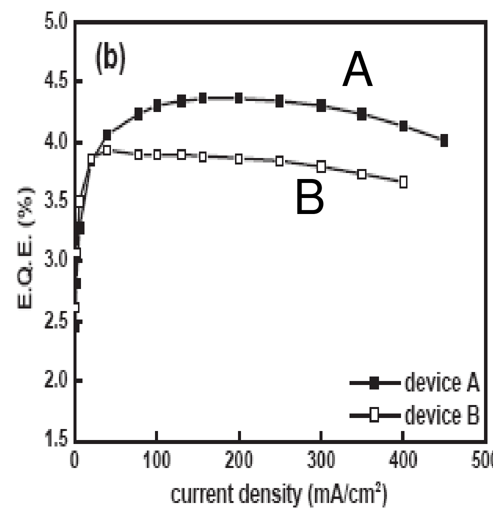
2-color B+G WOLED

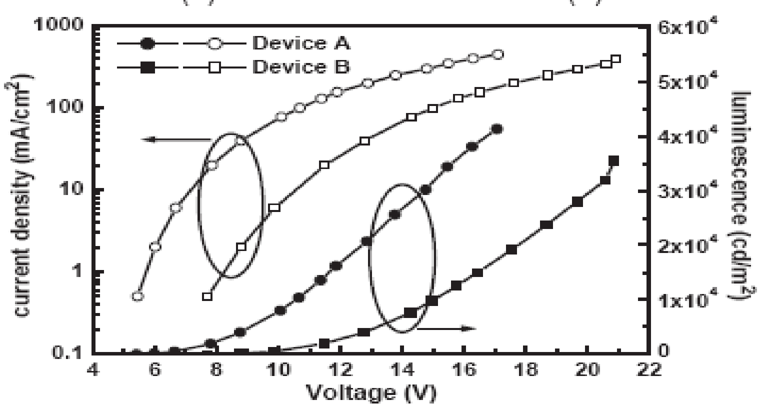












Device A is much better than Device B.

Y.S. Wu et al, Thin Solid Films 488(2005)265.

3-layer emission due to Bepp2, Alq3, Rubrene

Z.Y. Xie et al, APL, 74(1999) 641

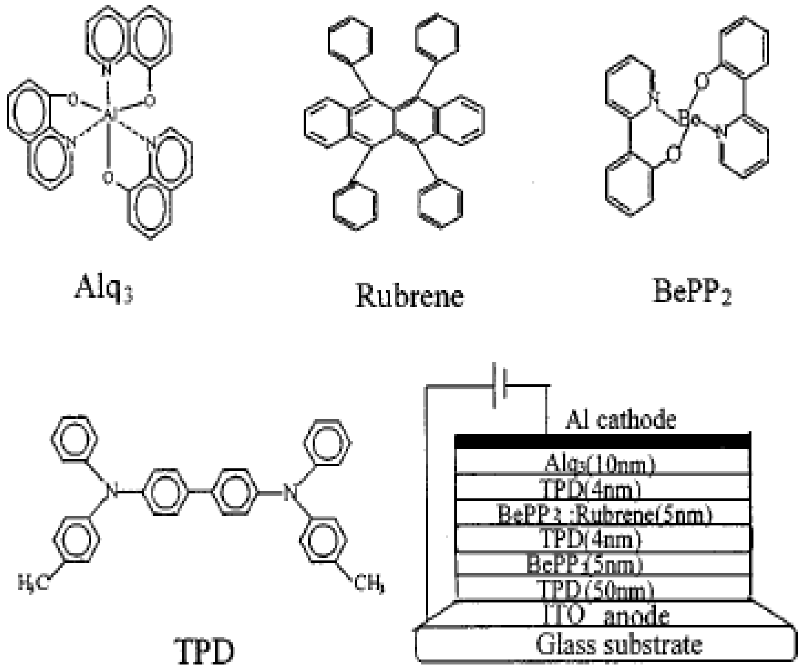
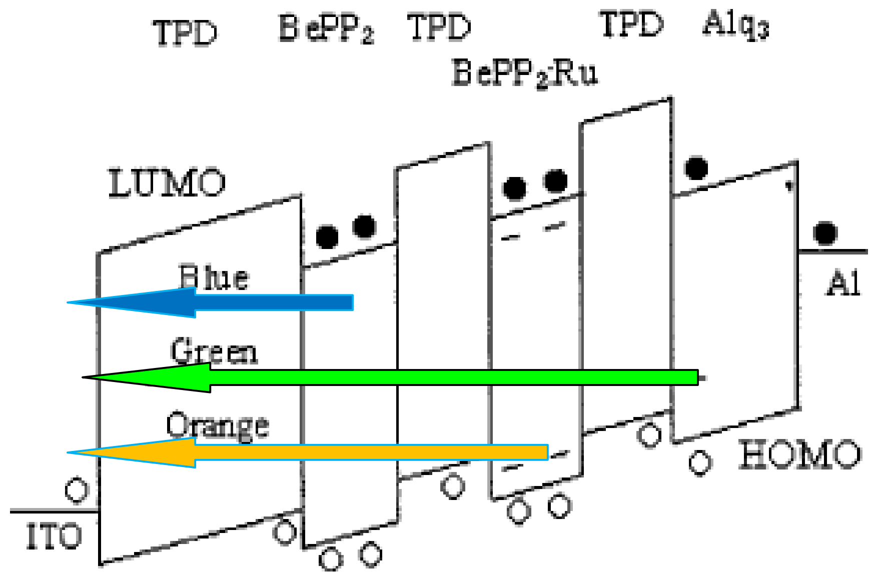


FIG. 1. Molecular structures of materials used and configuration for organic multiheterostructure white LEDs.



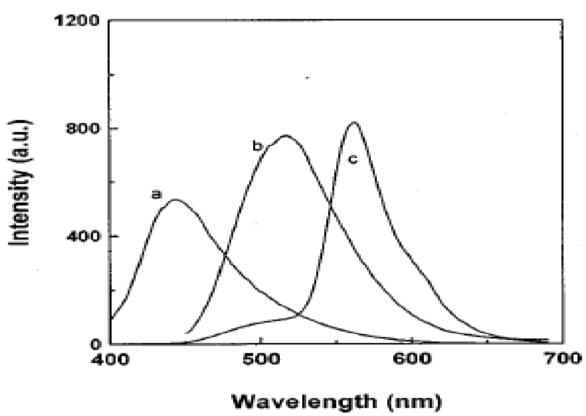


FIG. 2. EL spectra of (a) ITO/TPD(50 nm)/BePP$_2$(50 nm)/Al, (b) ITO/TPD(50 nm)/Alq$_3$(50 nm)/Al, (c) ITO/TPD(50 nm)/BePP$_2$:rubrene(50 nm)/Al, respectively.

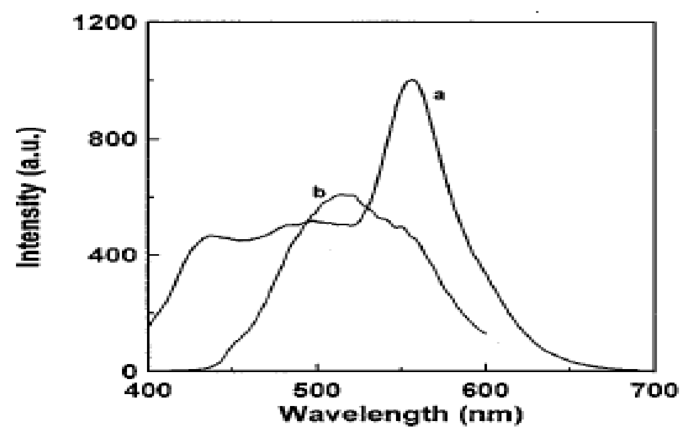


FIG. 4. EL spectra of (a) ITO/TPD(50 nm)/BePP$_2$(5 nm)/TPD(4 nm)/BePP$_2$:rubrene(5 nm)/TPD(4 nm)/Alq$_3$(10 nm)/Al and (b) ITO/TPD(50 nm)/BePP$_2$(5 nm)/TPD(8 nm)/BePP$_2$:rubrene(5 nm)/TPD(8 nm)/Alq$_3$(10 nm)/Al.

3-Layer emission

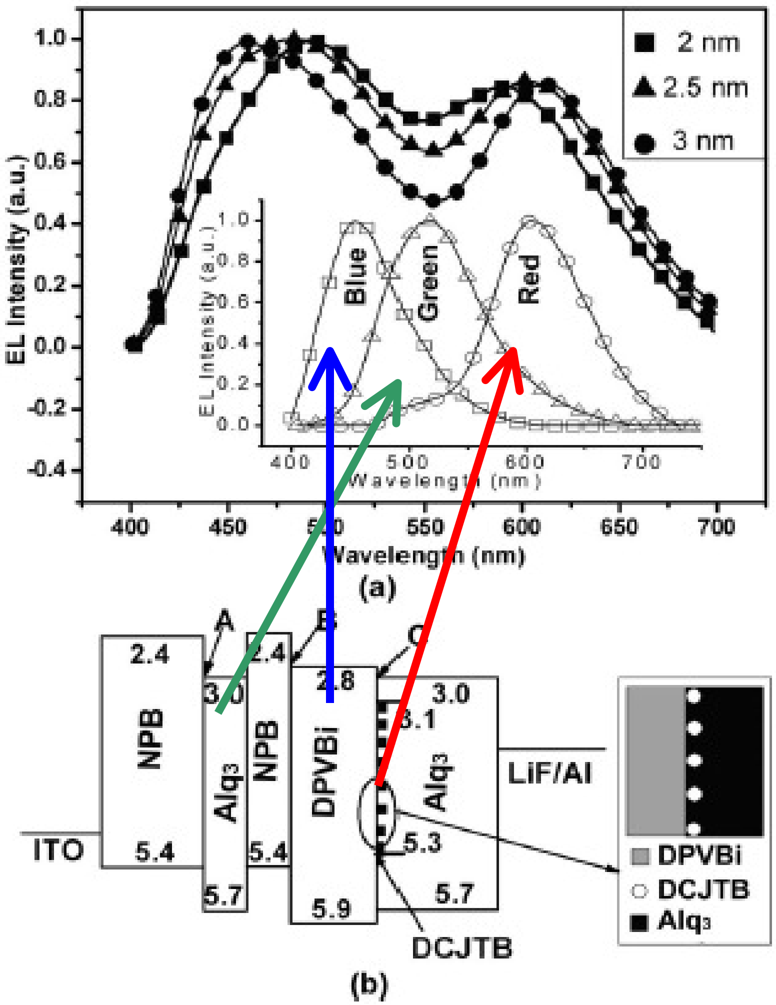


Fig. 1. (a) EL spectra of WOLED device with different thin-NPB layer thickness under the applied voltage of 8 V. The corresponding CIE-1931 *xy* coordinates are (0.329,0.368), (0.323,0.315), and (0.321, 0.290) when the thickness of the thin-NPB is 2, 2.5, and 3 nm, respectively. With increased bias, the CIE-1931 *xy* coordinates of the device with a 3 nm thin-NPB layer are located nearest to the coordinates (0.333, 0.333). Inset, EL spectra from DPVBi (□), Alq3 (△), and DCJTB (◦), which were obtained with

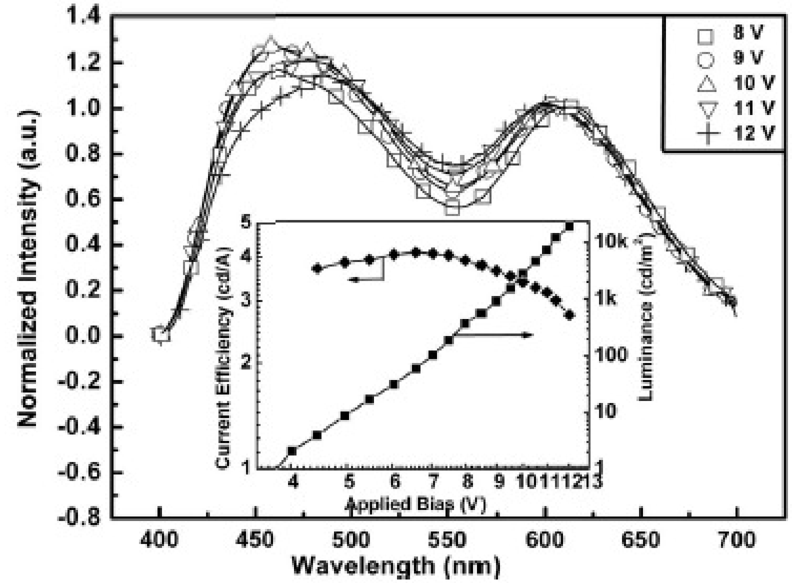


Fig. 2. EL spectra of the WOLED device with a 3 nm thick thin-NPB layer, which was applied at 8 V. Inset, luminance-efficiency–voltage characteristics.

CIE = (0.33, 0.33)

CCT(correlated color Temp.)= 2500-6000 K

CRI(color rendering index) > 80

Applied Bias (V)	CIE Coordinates x	y	CCT (K)	CRI
8	0.321	0.290	6014	80.9
9	0.315	0.299	6673	84.8
10	0.313	0.302	6714	85.8
11	0.318	0.320	6305	88.3
12	0.327	0.336	5804	90.2

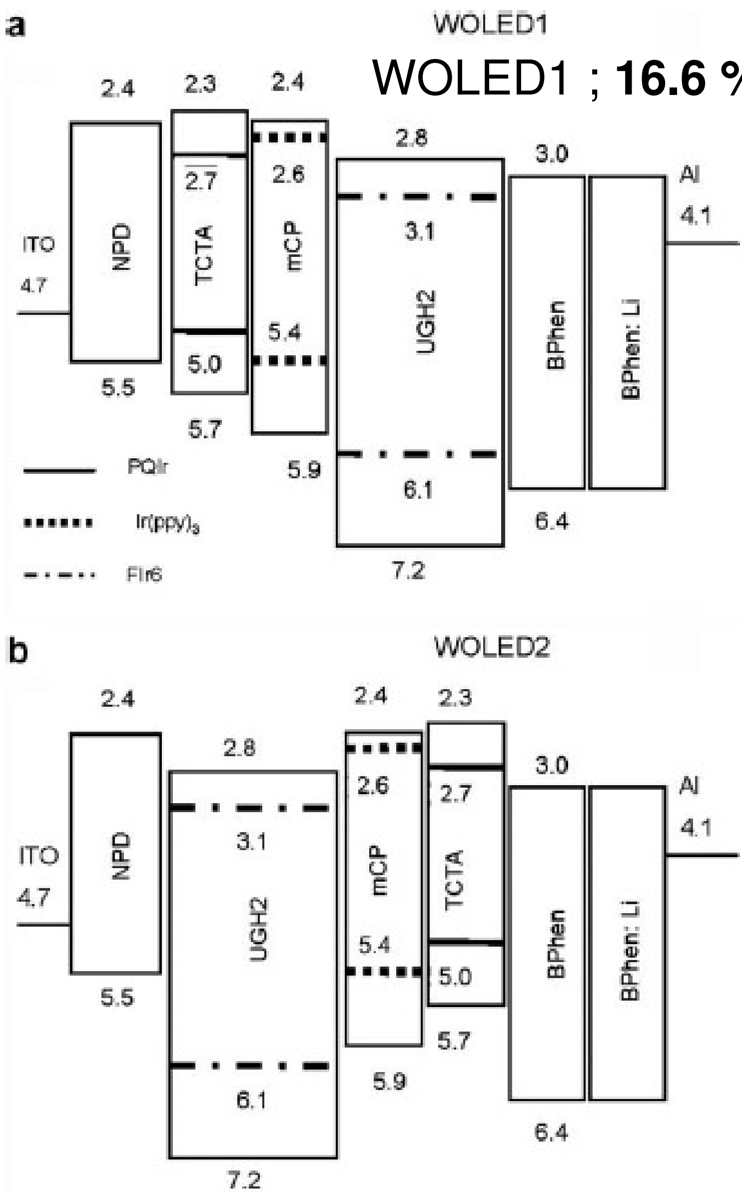
Zhu, Li, Tsuboi, et al, Opt. Lett. 32(2007) 3537.

High external efficiency from POLED with three small molecules

FIr6: bis(40,60-difluorophenylpyridinato) tetrakis(1-pyrazolyl)borate

PQIr: Ir(III) bis(2-phenylquinolyl-N,C20) acetylacetonate

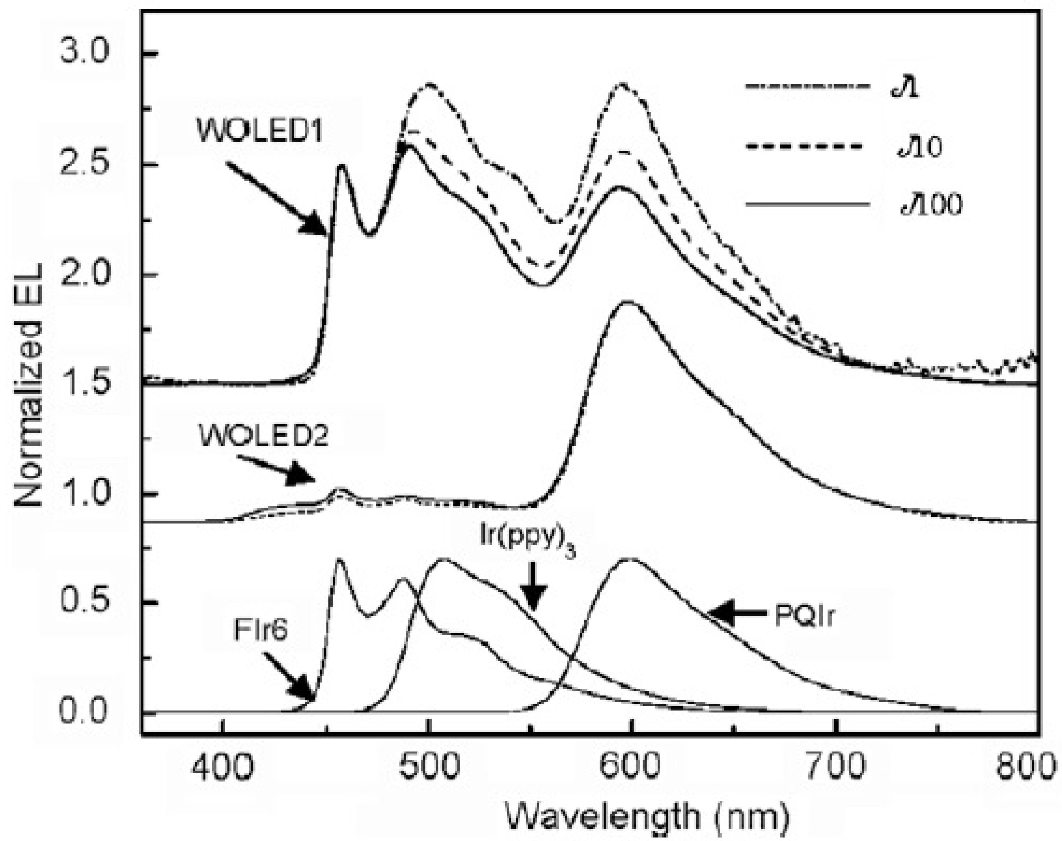
WOLED1 ; **16.6 %**



WOLED2; **6.0%**

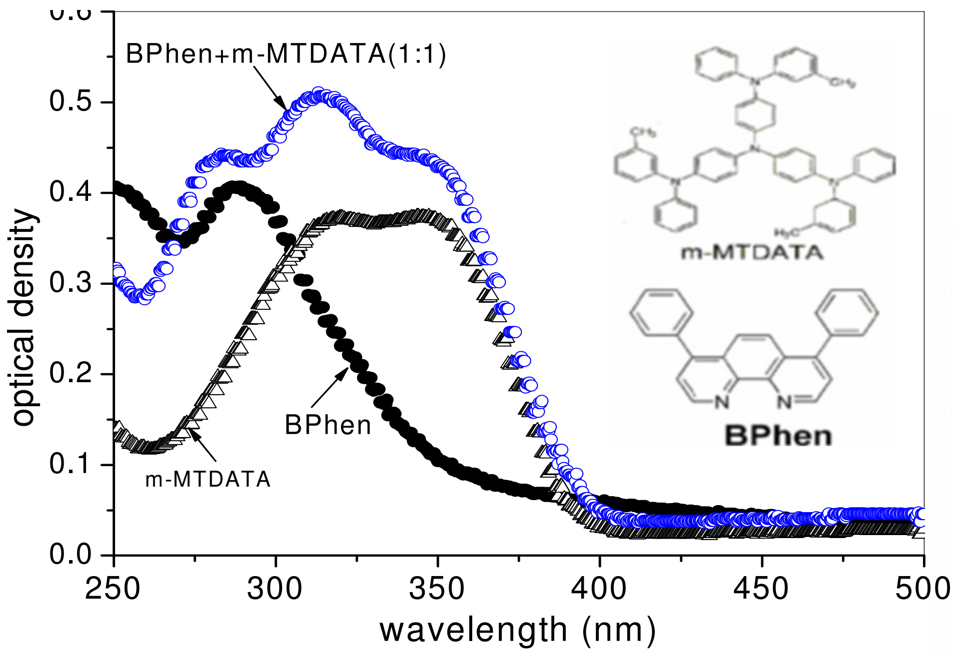
Reducing hole mobility for charge balance, Uniform distribution of holes and electron.

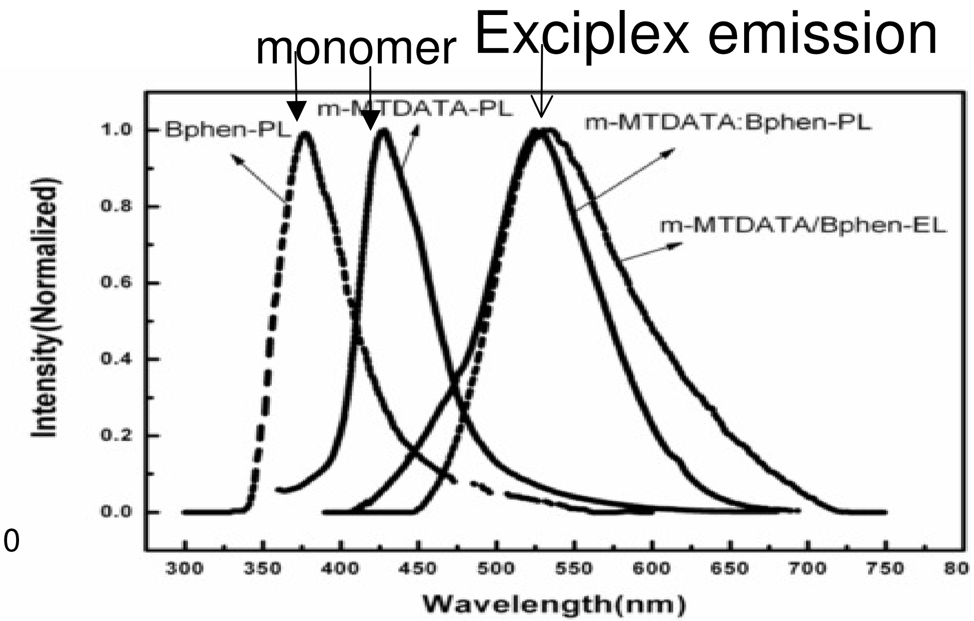
Ambipolar host for uniform exciton formation across the entire EML



Y. Sun, S.R. Forrest, Org. Electron.9 (2008) 994.

OLEDs with Exciplex emission





4,4',4"-tris[3-methylpheny-l(phenyl)amino] triphenylamine (m-MTDATA): hole-transport material :

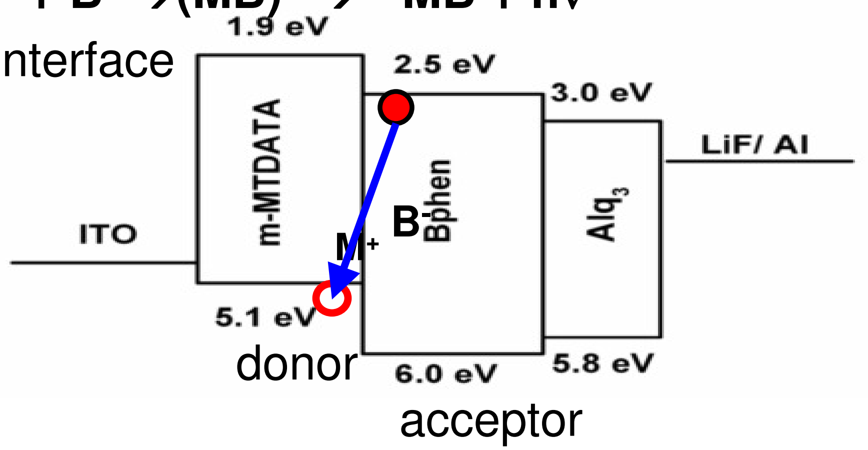
$M \rightarrow M^{+} + e$

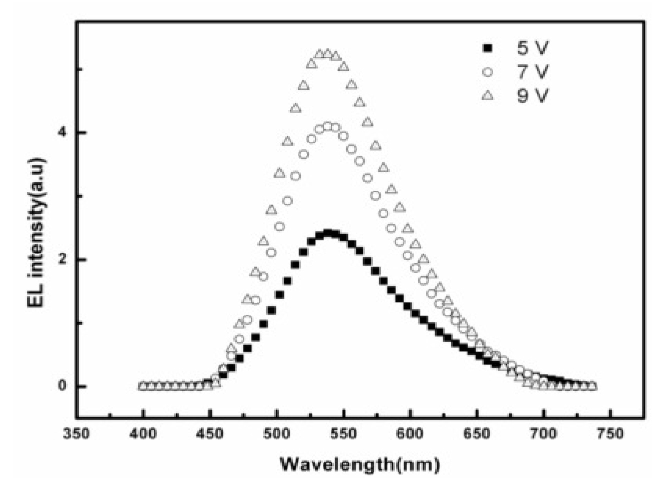
4,7 dipheny-1,10-phenanthroline (Bphen): electron-transport material : **$B + e \rightarrow B^{-}$**

6620cd/m² at 8.7V

$M^{+} + B^{-} \rightarrow (MB)^{*} \rightarrow MB + h\nu$

emission from interface

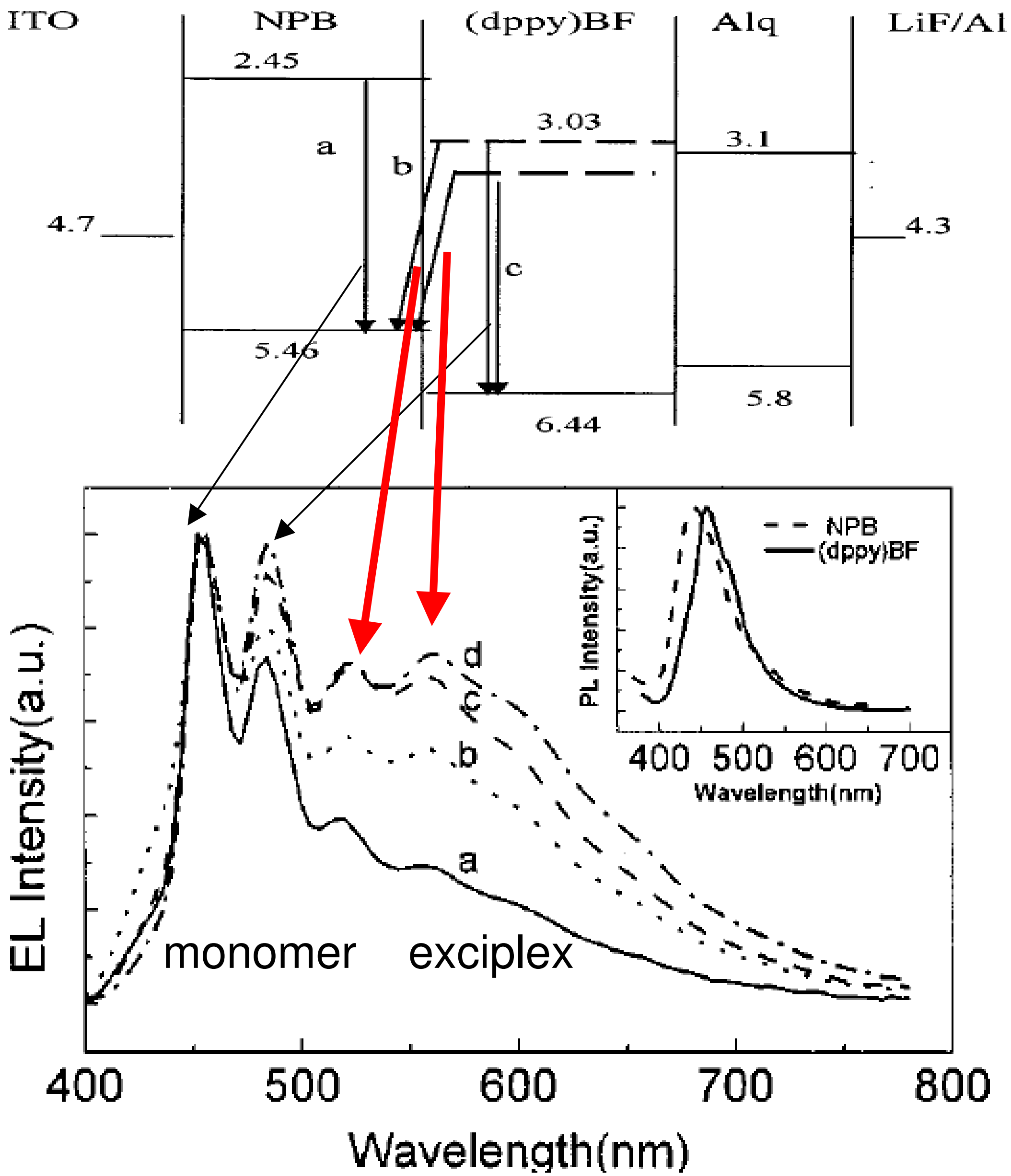


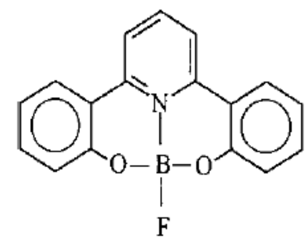


No emission from Bphen monomer

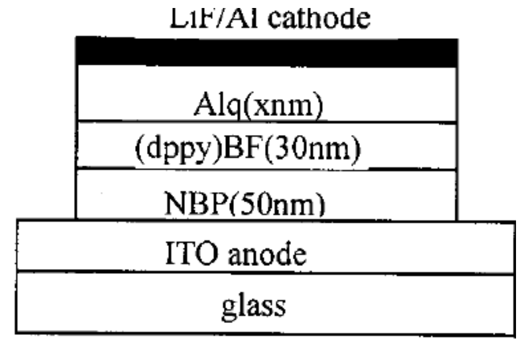
D. Wang, W.L.Li, T. Tsuboi et al, APL 92(2008)053304.

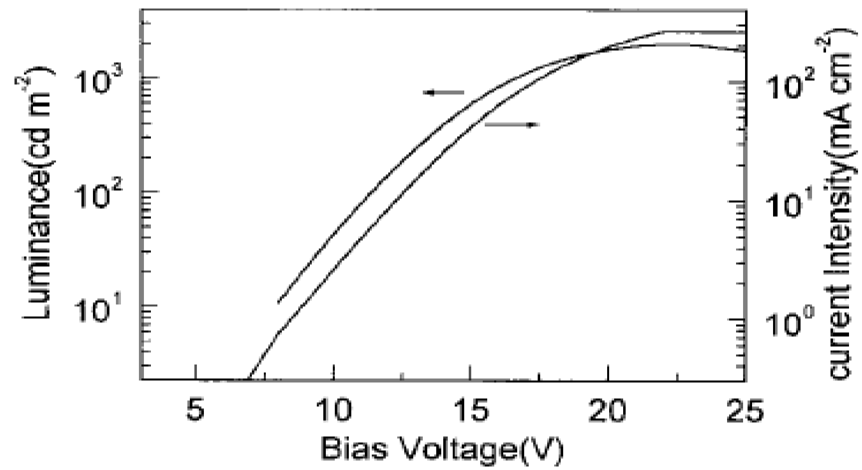
White OLED with exciplex and monomer





(dppy)BF

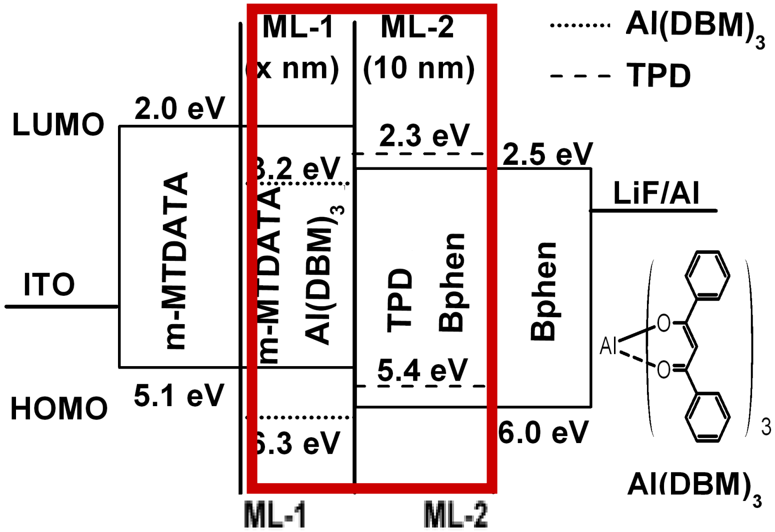


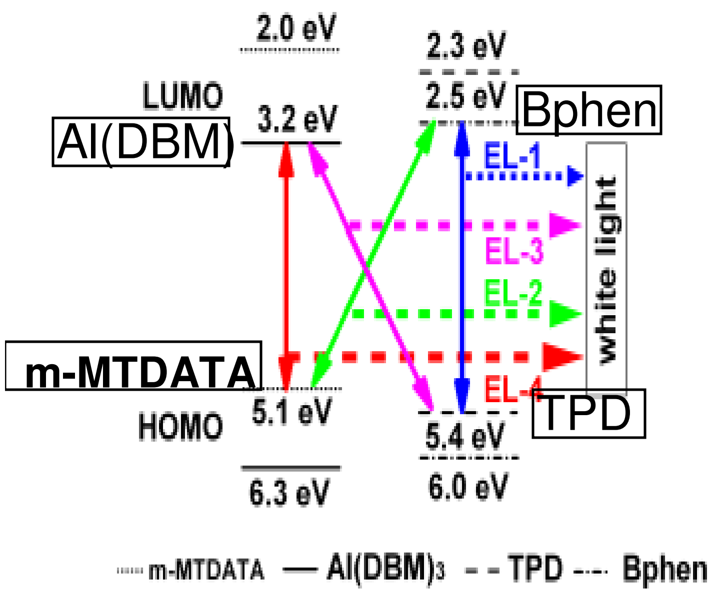


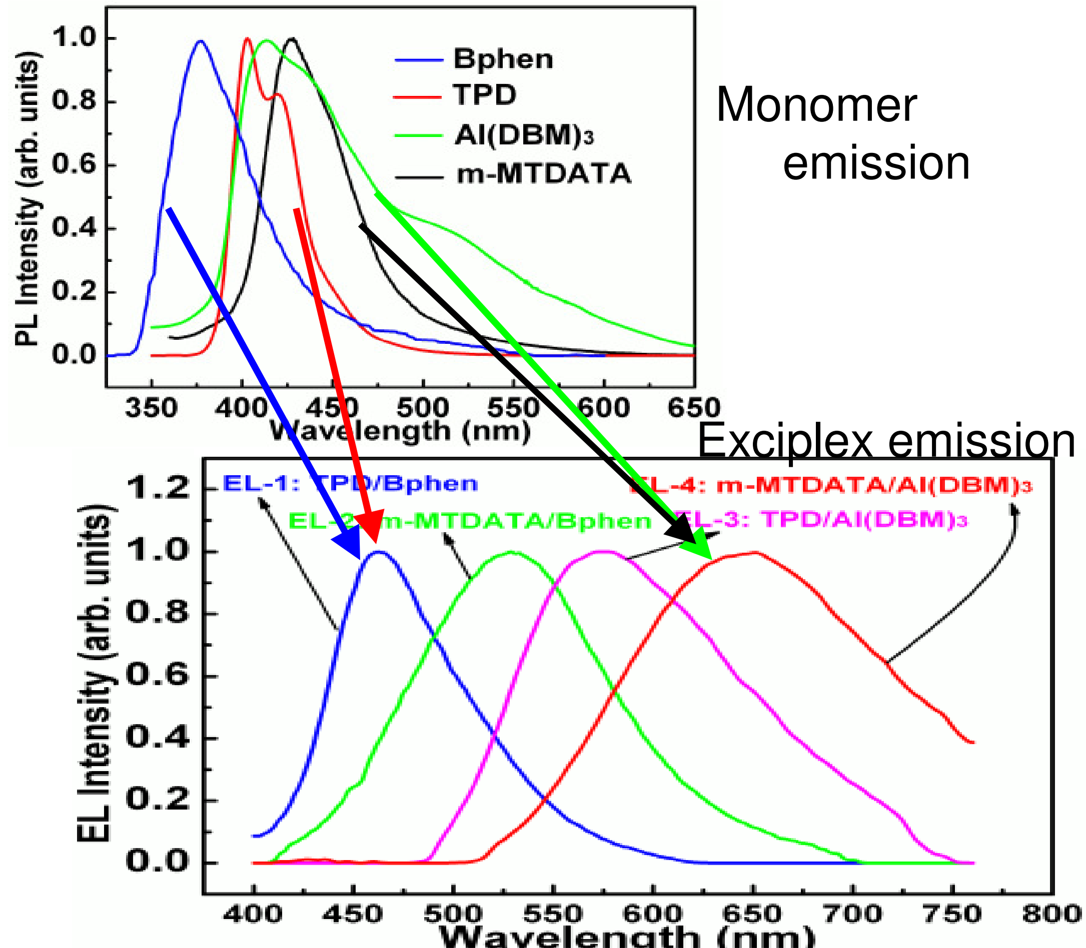
2000 cd/m^2
0.58 lm/W
CIE (0.31,0.35)

J. Feng et al, APL78 (2001) 3947.

White OLED using only exciplex



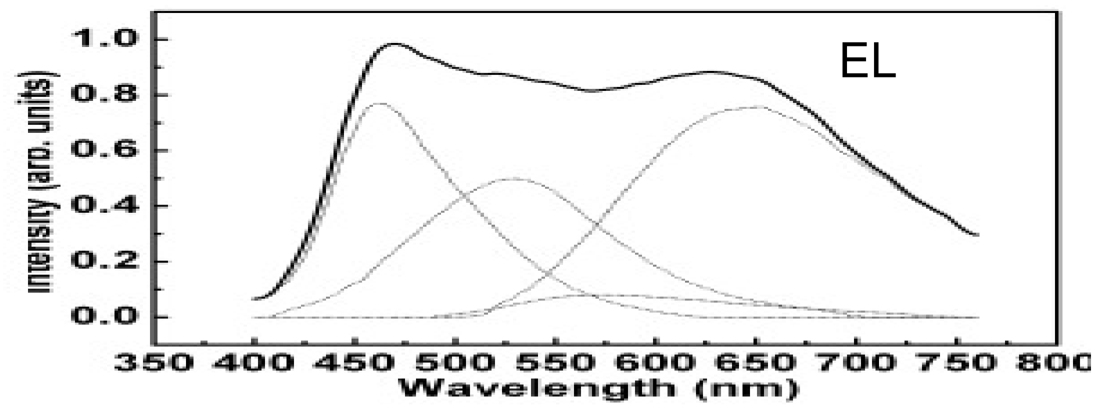




Monomer emission

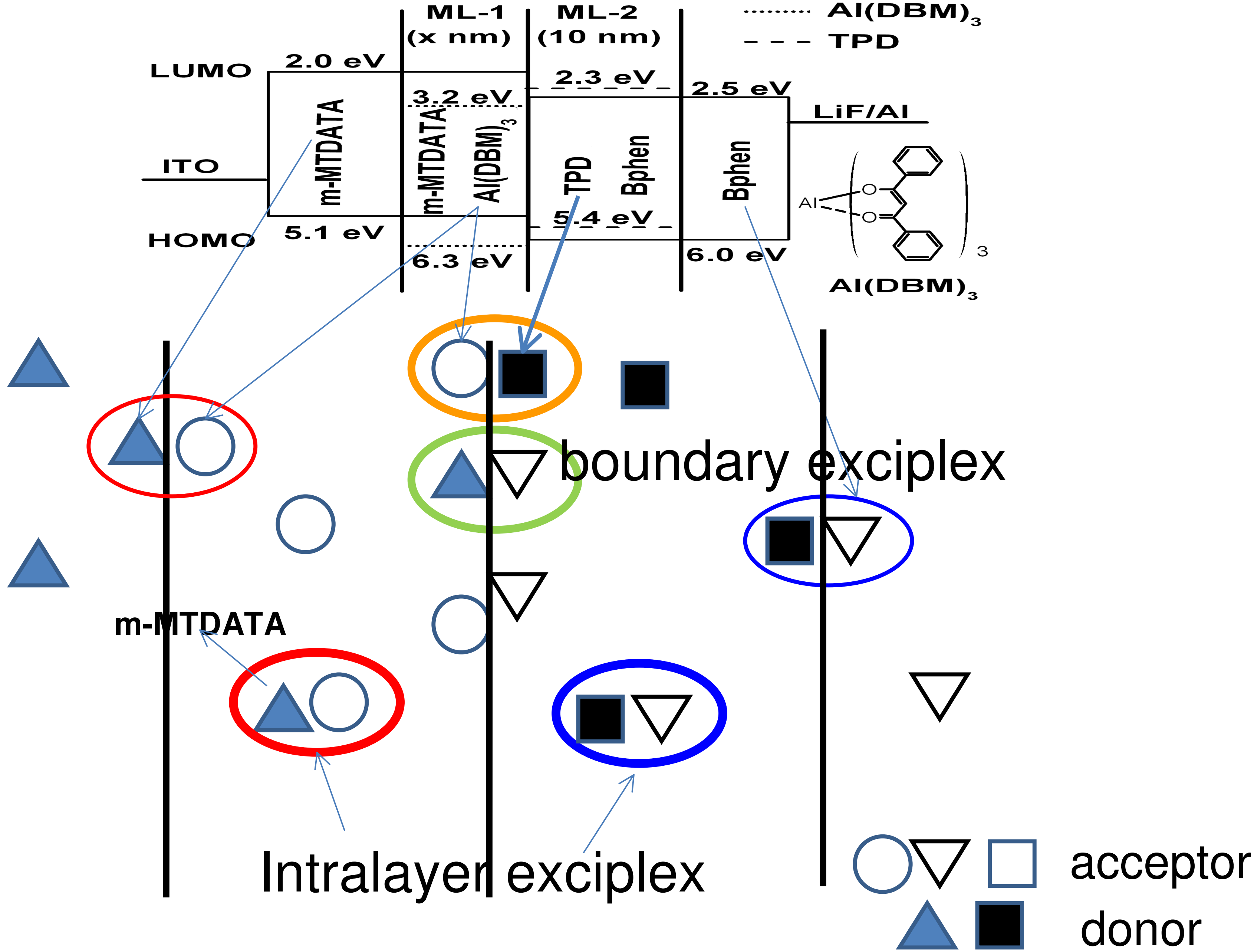
Exciplex emission

Very wide broad band

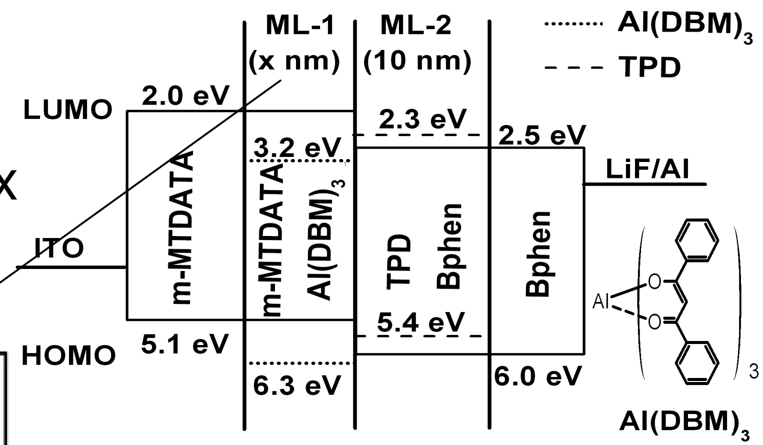


J.Z. Zhu, W.L. Li, T. Tsuboi, et al, to be published.

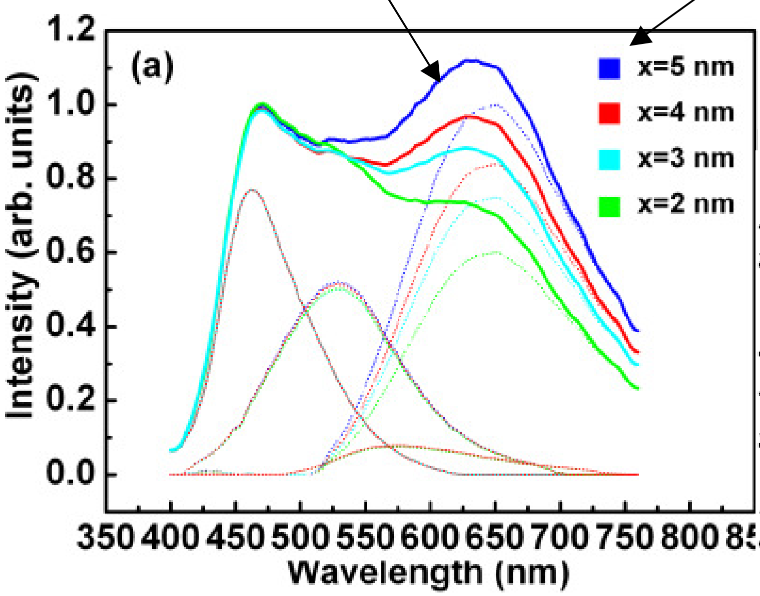
Four exciplexes in a device

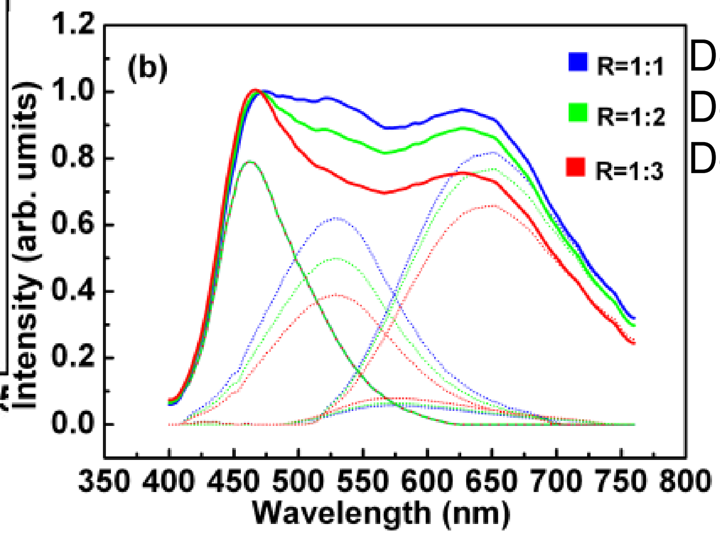


Increase of Intralayer exciplex



R=
M-MTDATA:Al(DBM)$_3$





Decrease of R:
Decrease of m-MTDATA
Decrease of red exciplex

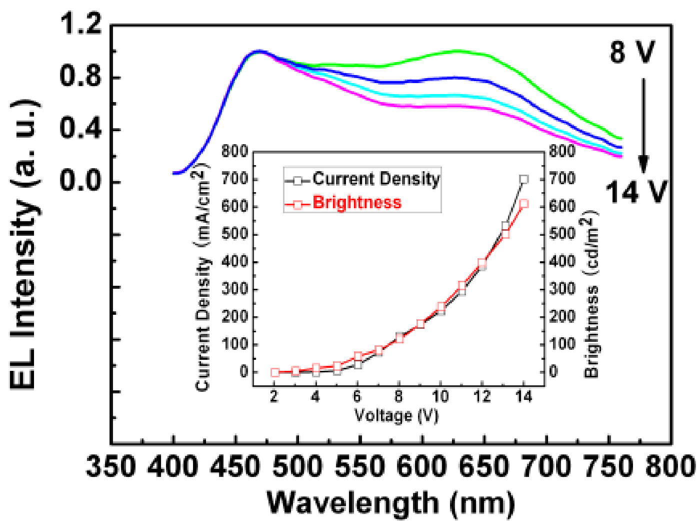


Table 1 CIE coordinates, CCT, and CRI of the WOLED device with x=3 nm and R=1

Bias voltage (V)	CIE coordinates (x, y)	CCT (K)	CRI
8	(0.36, 0.37)	4593	94.0
10	(0.33, 0.35)	5477	94.1
12	(0.32, 0.35)	6100	93.6
14	(0.31, 0.35)	6571	92.5

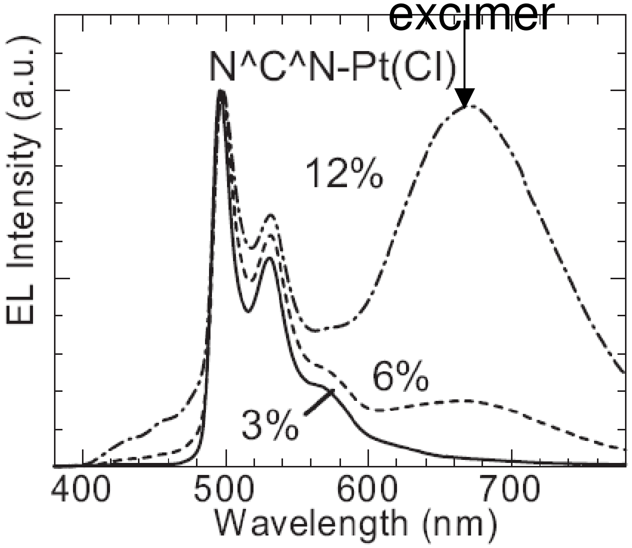
Multi-coloration by single molecule

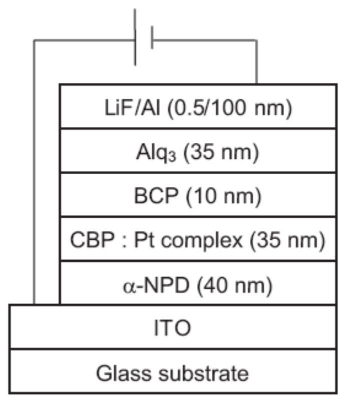
Excimer

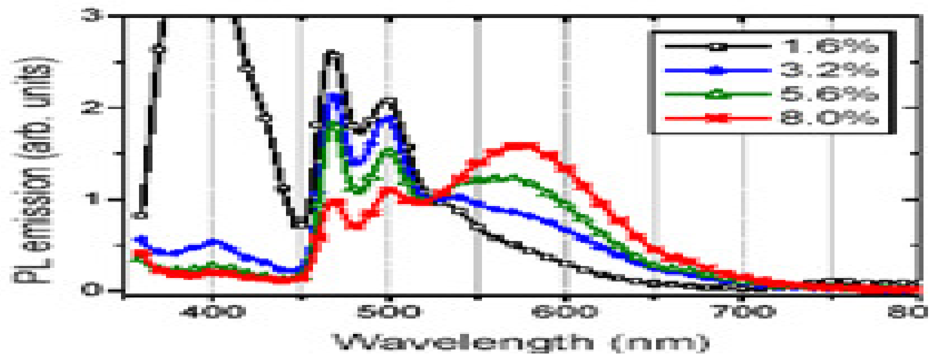
Mixed ligand molecule

Single dopant WOLED with Excimer emission

M*M ⟶ M + M + hυ

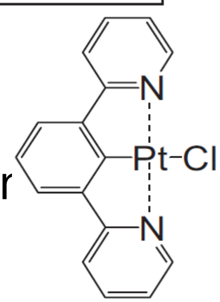




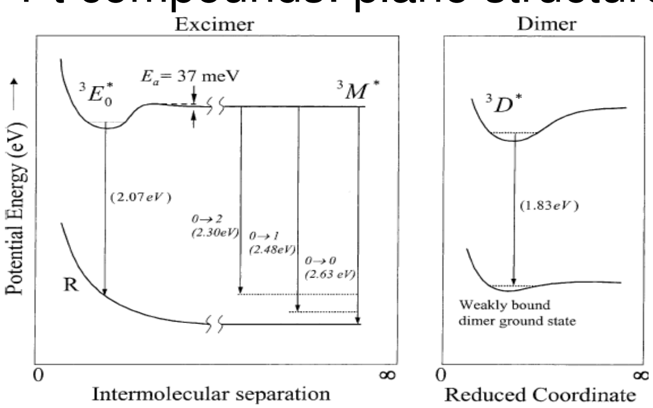


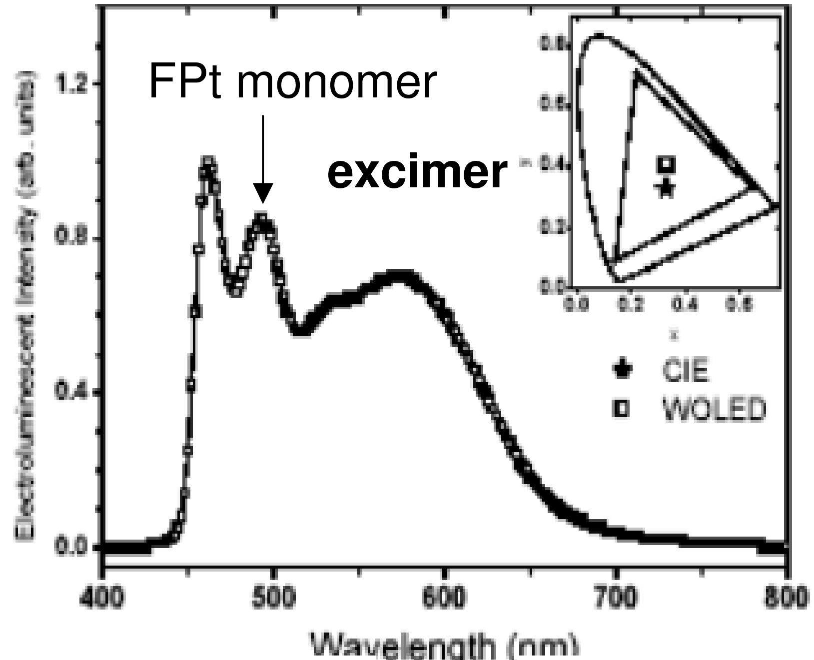
*T. Tsuzuki, S. Tokito, Proc. Int. Super-Functionality Organic Devices, IPAP Conf. Series 6 (2005) 99.

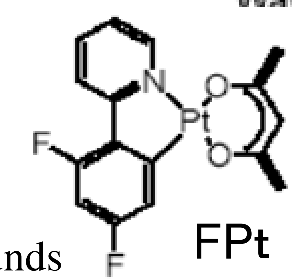
Pt compounds: plane structure, stackir



N^C^N-Pt(Cl)

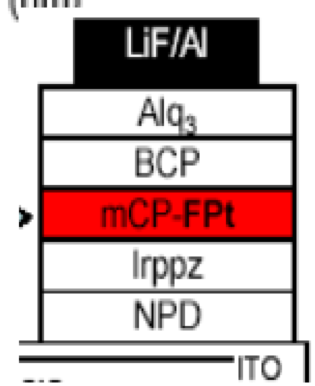






FPt

cyclometalated Pt^{2+}-compounds



QE= 6.1% , CRI=73, CIE=(0.32, 0.39), 11.8 lm/W (at 1cd/m2)

V. Adamovich et al, New J. Chem. 26 (2002) 1171.

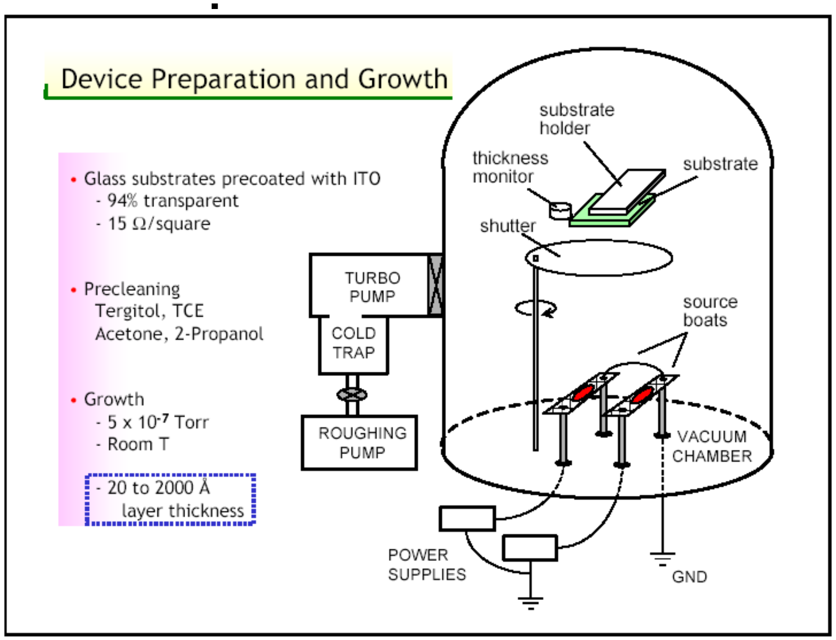
polymer or small molecule ?

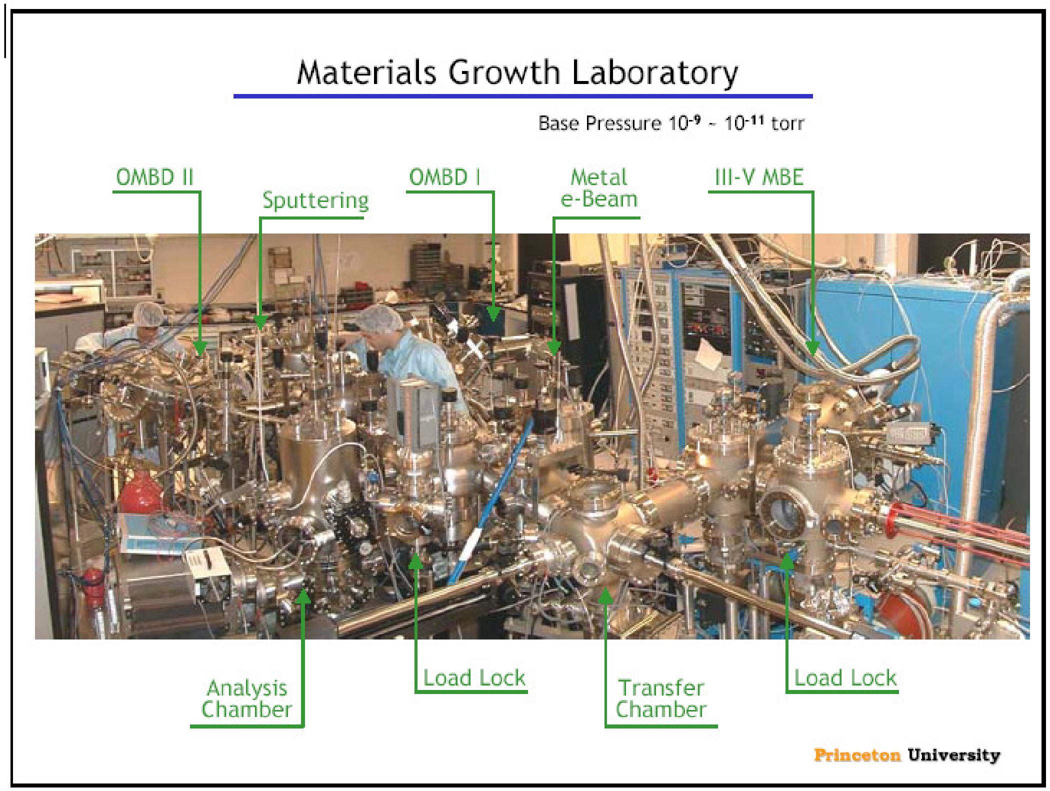
Polymer:

spin-coating, wet-process: cheap, easy, simple structure (2-layer), and ink-jet possible (for mass-production)

Small molecule:

thermal evaporation in





Polymer White OLEDs

A. Dispersion type（doping, blend, guest-host）

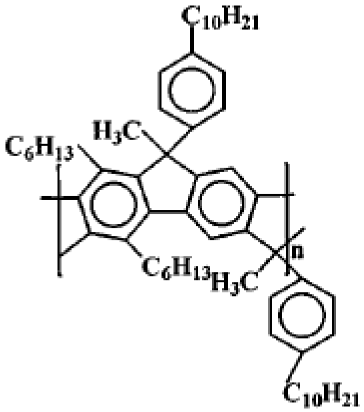
dopant	**host**	emitter
FL small molecule	FL polymer	**Dopant**
PL small molecule	FL polymer	**Dopant**
FL polymer	FL polymer	**Dopant**
PL polymer	FL polymer	Dopant+host
PL polymer	PL polymer	Dopnat+host

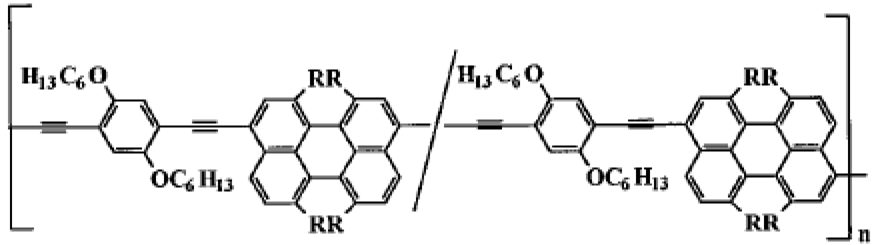
FL: Fluorescent
PL: Phosphorescent

B. Single polymer

	emitter	
Non-copolymer	Monomer+Excimer	FL polymer
Non-copolymer	Monomer+Electromer	FL polymer
Blended in backbone, copolymer	Monomer	PL polymer
Blended in side-chain, copolymer	Monomer	PL polymer

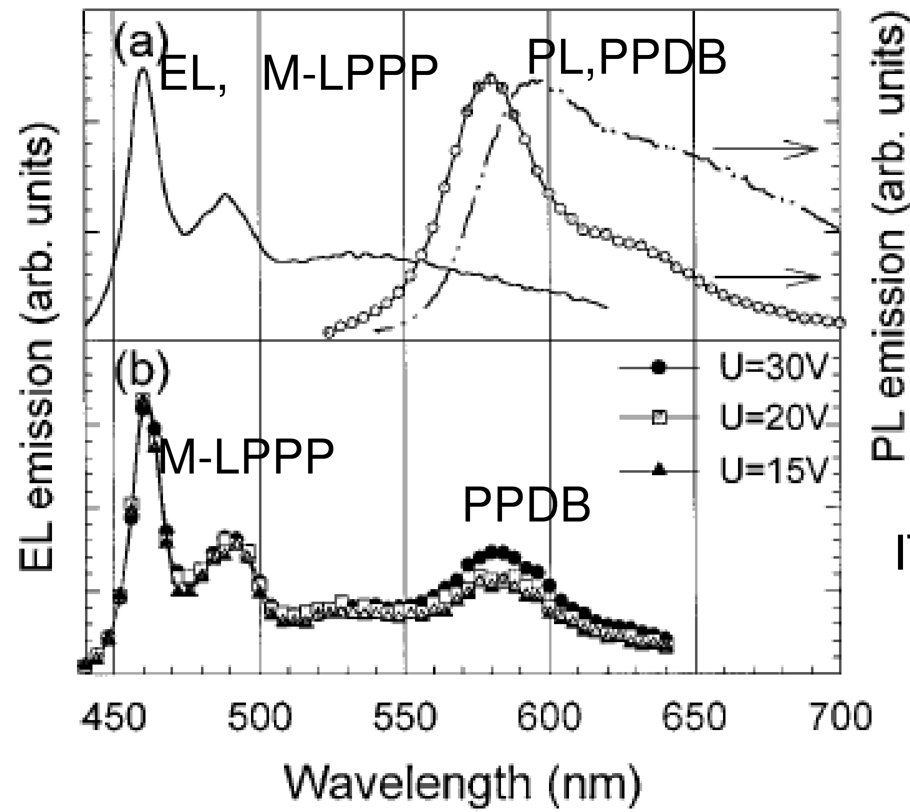
Guest polymer ＋ host polymer





0.05wt% PPDB（polyperiren-ethylbenzen)dopant

m-LPPP(ladder-type paraphenyrene)
host

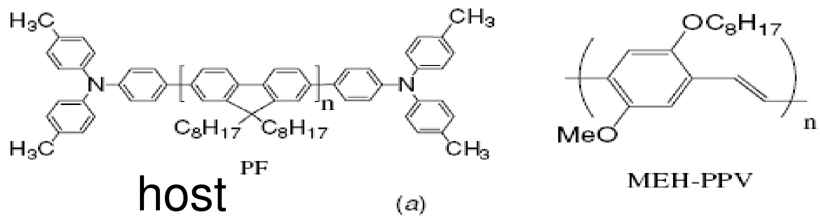


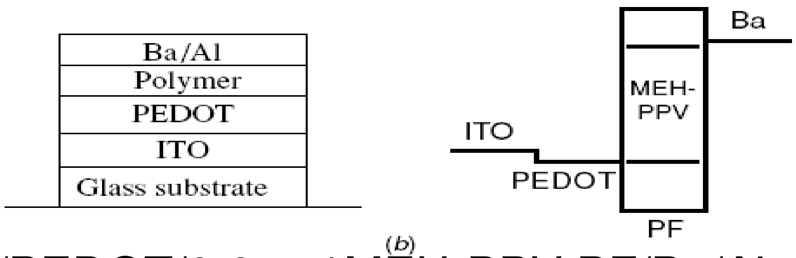
Ext. Effic: 1.2 %,
CIE(0.31, 0.33)

ITO/ 0.05%PPDB:m-LPPP /Al

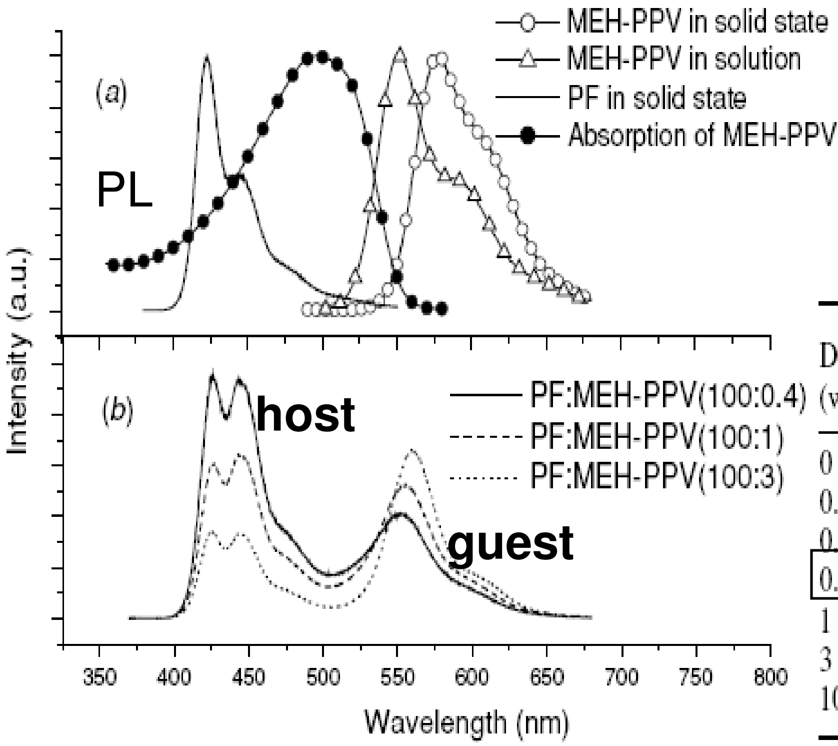
S. Tasch et al, APL 71(1997)2883.

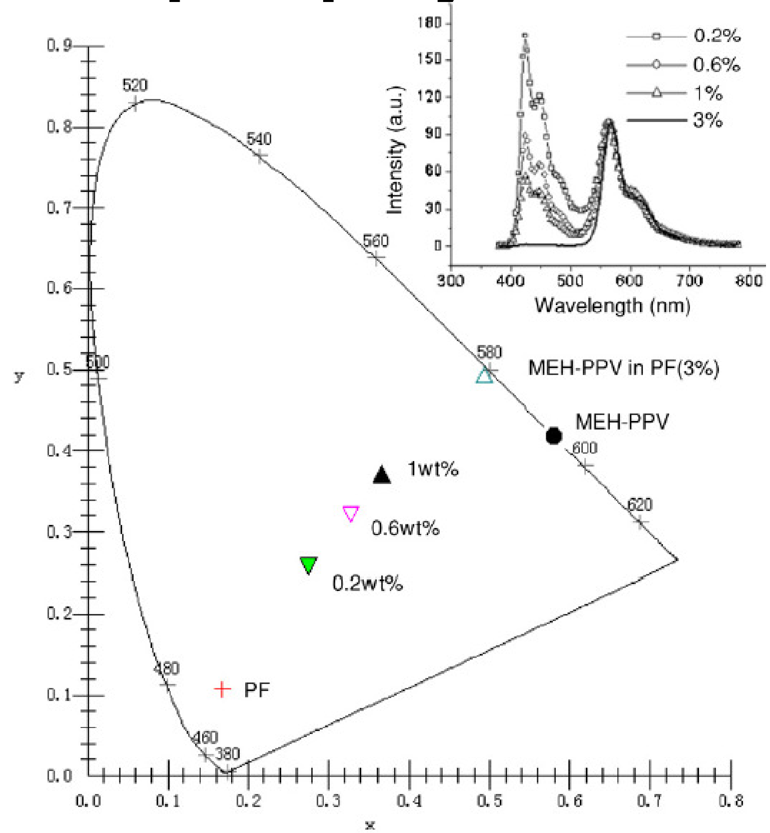
Doped WPLED: Polymer-doped polymer





ITO/PEDOT/0.6wt%MEH-PPV:PF/Ba/Al



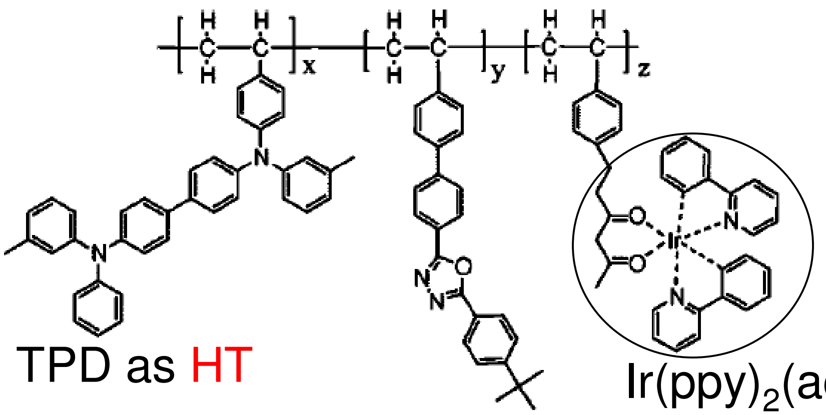


Doping level (wt%)	Max efficiency η_{ex} (%)	Max efficiency (cd A^{-1})	Max luminance (cd m^{-2})	Turn-on voltage (V)	CIE(*x*, *y*) (at 7 V)
0 (pure PF)	0.45	0.664 at 9 V	1444 at 10 V	5	(0.17, 0.11)
0.2	0.28	0.533 at 7 V	1067 at 9 V	5	(0.28, 0.26)
0.4	0.45	0.921 at 5 V	5728 at 10 V	4	(0.29, 0.27)
0.6	0.95	2.318 at 4 V	10 270 at 10 V	4	(0.33, 0.31)
1	0.38	0.925 at 5 V	10 990 at 10 V	4	(0.37, 0.38)
3	0.28	0.885 at 8 V	1984 at 11 V	5	(0.49, 0.50)
100 (pure MEH-PPV)	0.46	0.869 at 8 V	505 at 8 V	5	(0.57, 0.43)

F.Z. Shen et al, Semicon. Sci. Technol. 21(2006)L16. Ext. Effic: 0.95 %

Carrier balanced green polymer

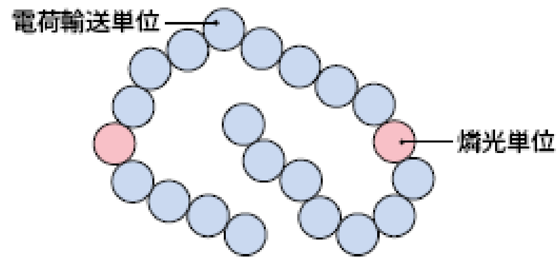
M. Suzuki (NHK) et al, APL 86(2005)103507

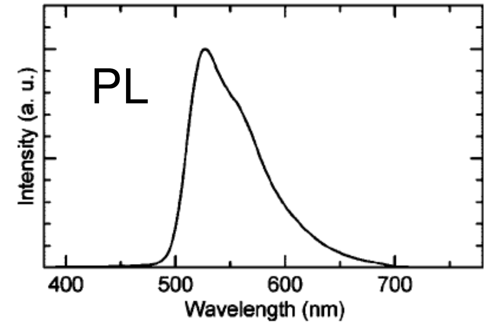


TPD as HT

PBD as ET

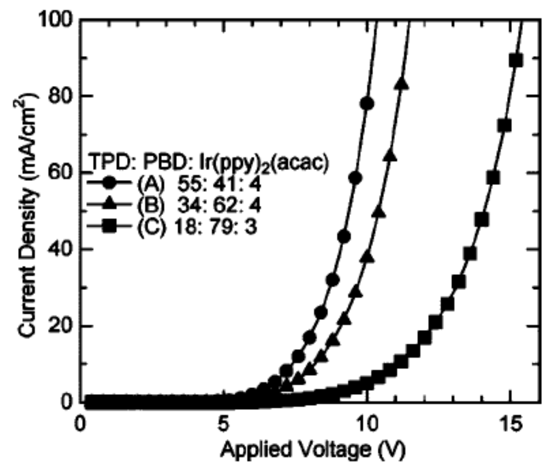
$Ir(ppy)_2(acac)$ as EL





TPD:PBD:$Ir(ppy)_2(acac)$=
(A)55:41:4, (B)36:62:4, (C)18:79:3 濃度比が重要

η_{ext}=11.8% at 0.12mA/cm2,
power effi.= 38.6 lm/W at 0.02mA/cm2
with Cs e-injector



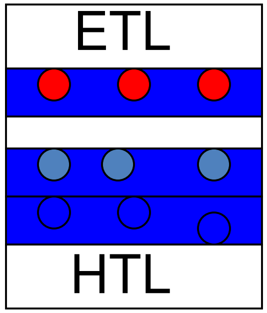
Polymer	TPD: PBD: $Ir(ppy)_2(acac)$	Electron-injection layer	$\eta_{ext}(\%)^a$	$\eta_{power}(lm/W)^a$
A	55: 41: 4	Ca	1.0	1.3
B	34: 62: 4	Ca	3.9	6.3
C	18: 79: 3	Ca	6.8	11.6
C	18: 79: 3	Ba	9.7	19.4
C	18: 79: 3	Cs	11.8	38.6

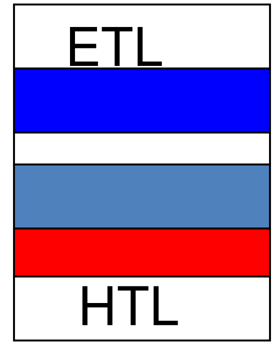
[a]Maximum value.

c.f. S. Lamansky et al, JACS123('01)4304:
$Ir(ppy)_2(acac)$ in CBP host, multi-layer OLED
12.3%, 38 lm/W, >50 Cd/A

Guest-Host system or Non-doped system ?

White OLEDs





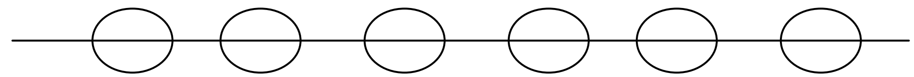
Non-dopant system is much better than guest-host system

Because

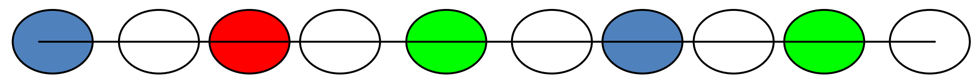
1. Best concentration is 1-2% dopant, difficult to control it within ±0.5% in mass produced OLEDs
2. For White OLED, blue-green-red stacking layered OLED gives rise to energy transfer from blue to green to red layer、color instability

Single polymer WOLEDs

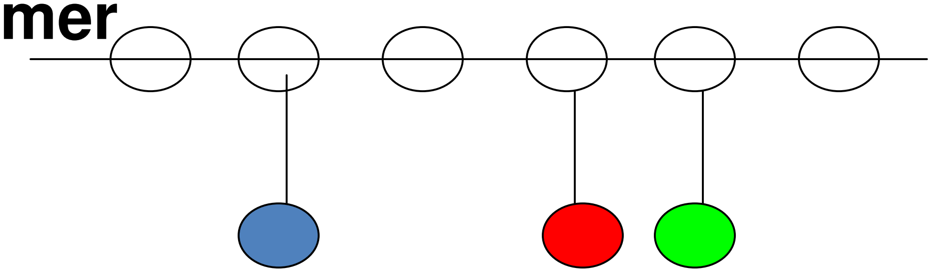
polymer



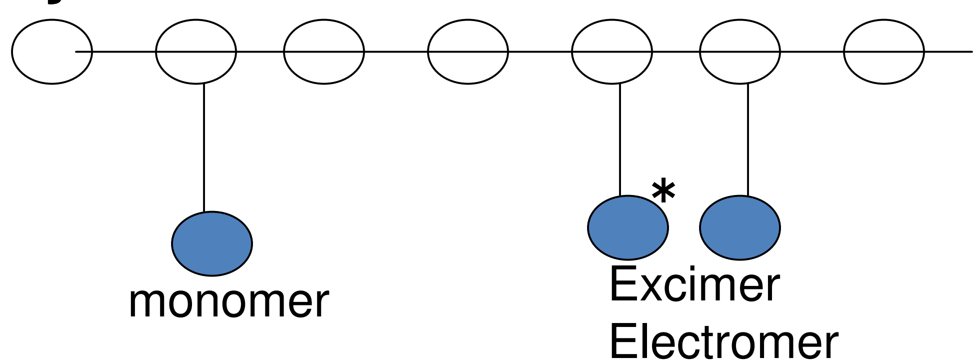
Backbone copolymer



Side-chain copolymer



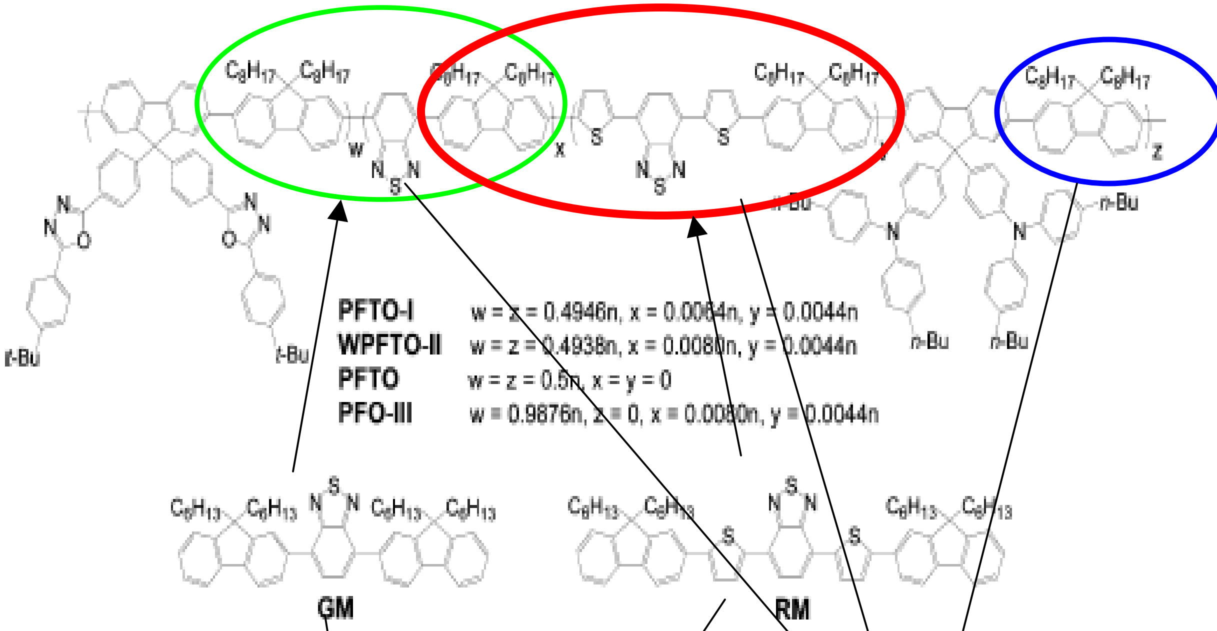
Mono-dopant polymer



Single backbone copolymer

C.Y. Chuang et al, Macromol.40(2007)247

PF:Polyfluoren,
a bipolar charge-tranporting PF derivative



4,7-Bis(9,9-dihexylfluoren-2-yl)-2,1,3-benzothiadiazole (GM)

単一高分子型

4,7-Bis[5-(9,9-dihexylfluoren-2-yl)thiophen-2-yl]-2,1,3-benzothiadiazole (RM). Using the procedure described for GM, the

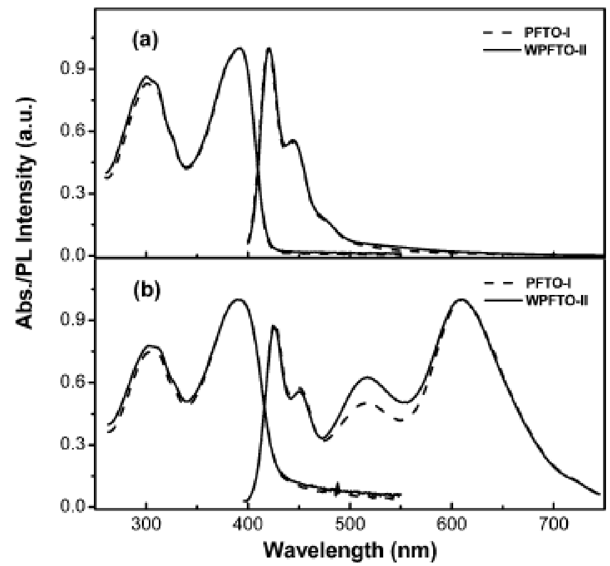


Figure 2. Absorption and PL spectra of **PFTO-I** and **WPFTO-I** (a) dilute $CHCl_3$ solutions and (b) the solid state.

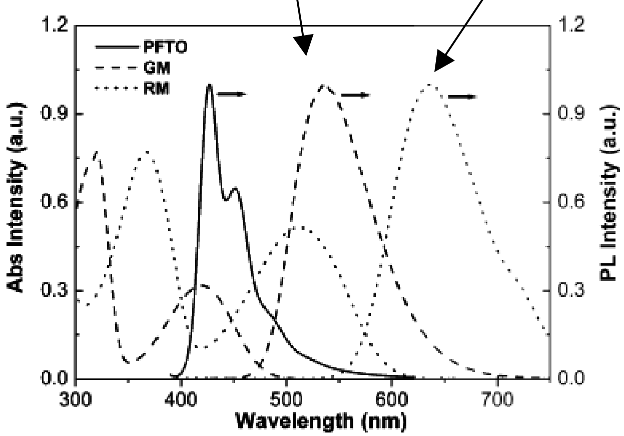
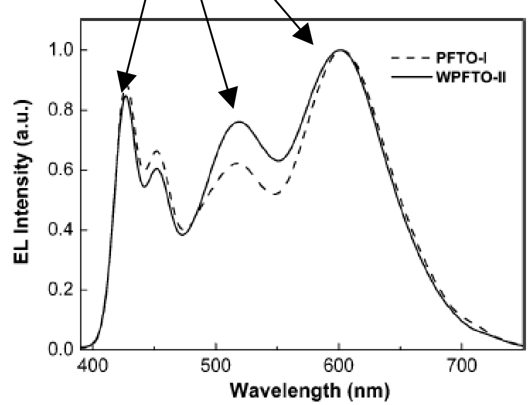
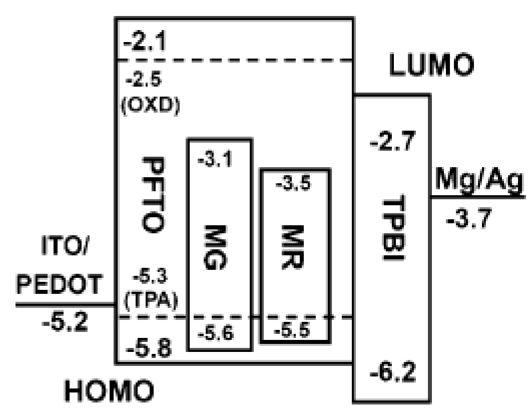


Figure 3. PL spectrum of **PFTO** in the solid state and the PL and absorption spectra of **GM** and **RM** in dilute $CHCl_3$ solutions.



4. EL spectra of the devices incorporating PFTO-I or WPFTO-
ıe emitting layer at an applied potential of 9 V.



backbone copolymer D.Ma

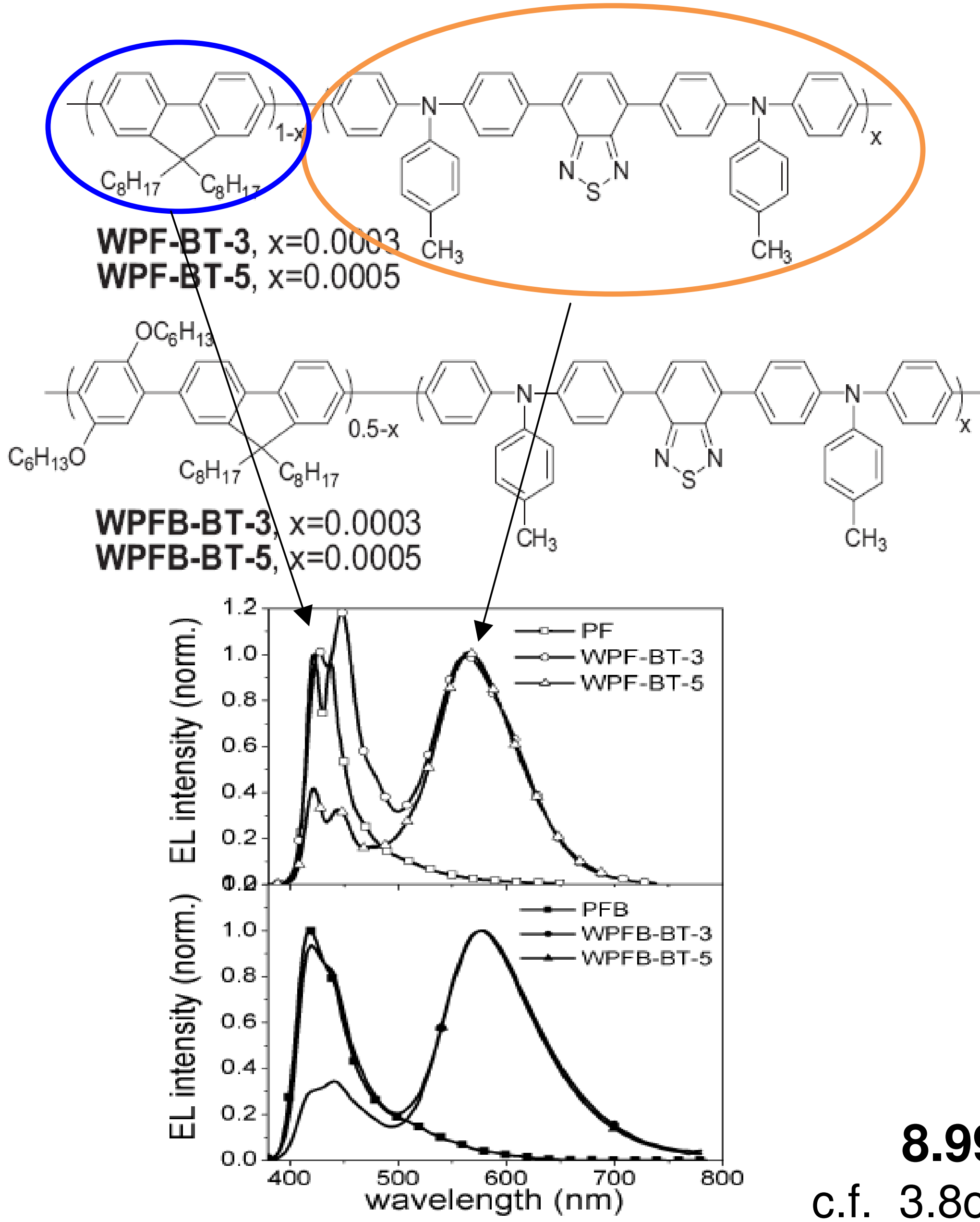
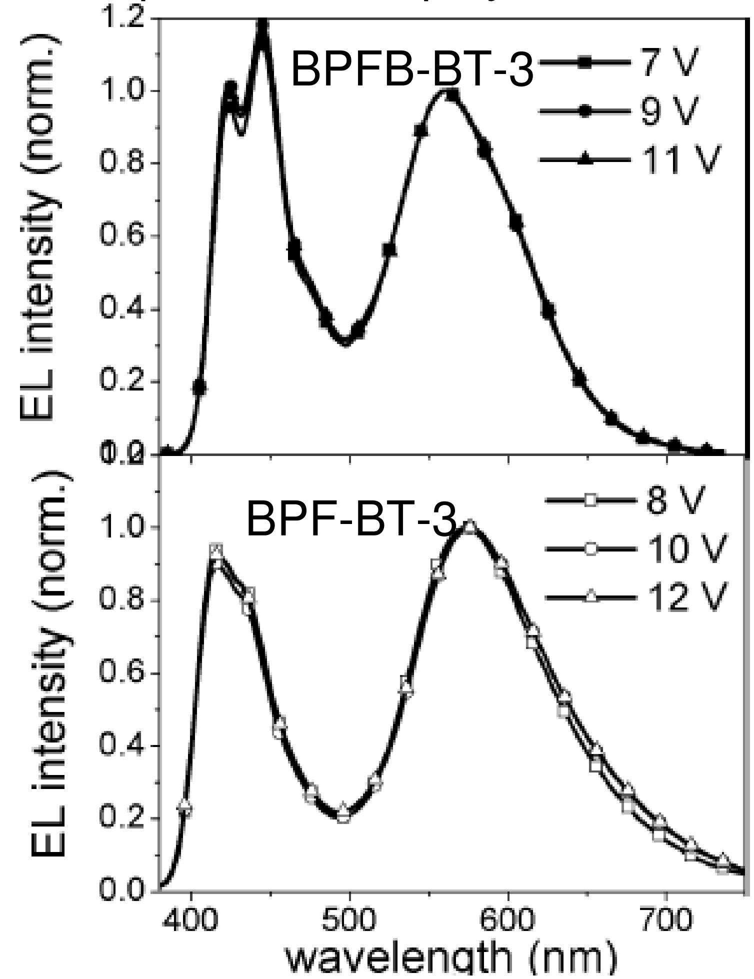


Figure 5. Electroluminescence spectra of single layer devices (ITO/PEDOT:PSS/polymer/Ca/Al) of the polymers.

Different dopant:
red-emitter2,1,3-benzothiadiazole-incorporated blue-polymer



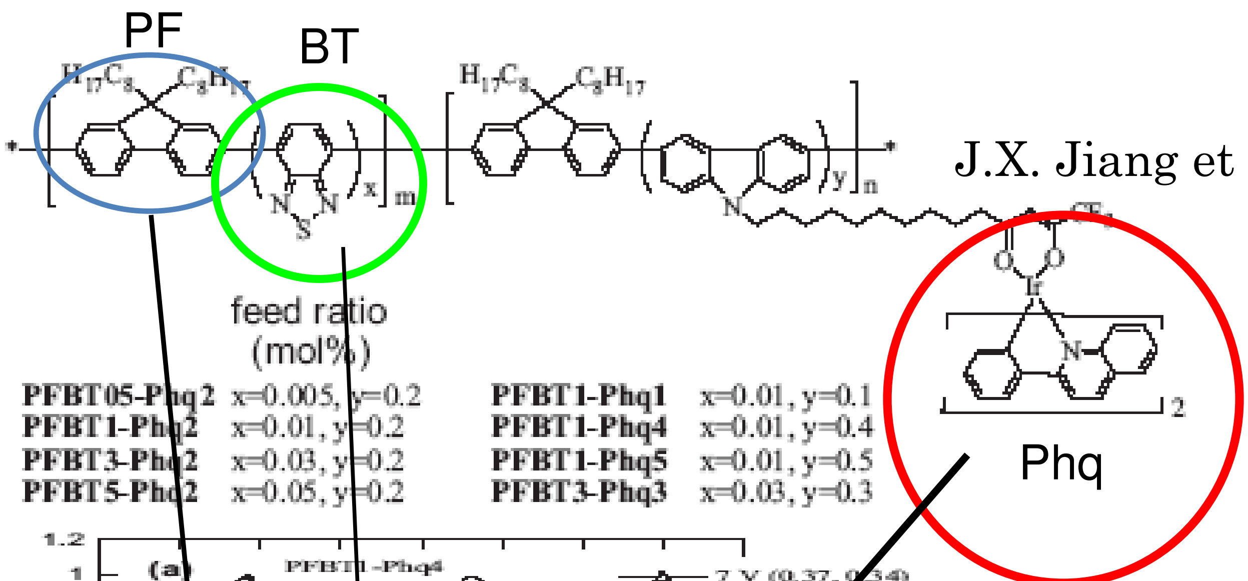
8.99cd/A, 5.75lm/W, η=3.8%

c.f. 3.8cd/A, 2.0lm/W, η=1.50%

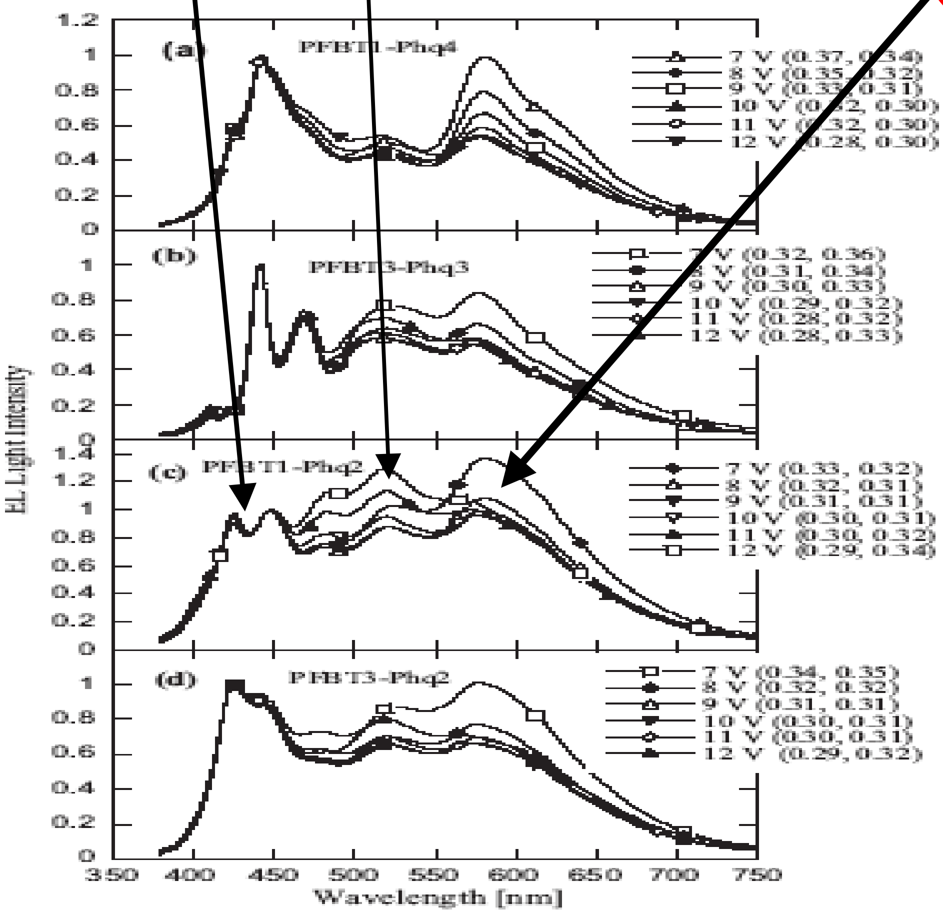
J. Liu et al, Adv. Func. Mat. 16(2006)957.

FL+PL

J.X. Jiang et al, Adv. Mater. 18(2006)1769.



Phosphorescence

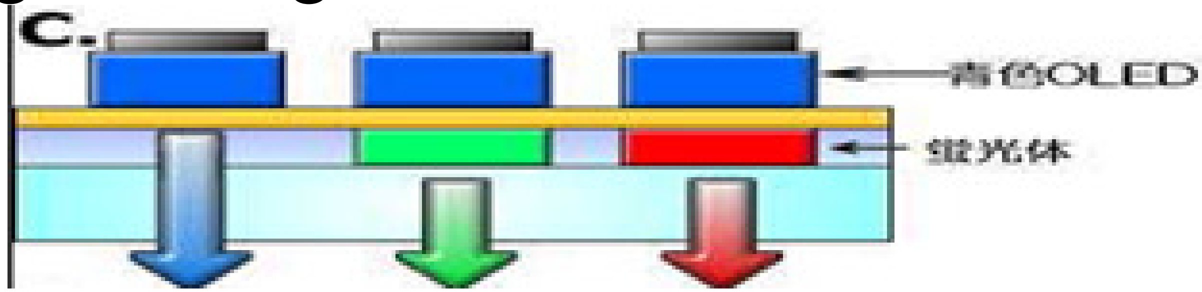


赤色発光： フェニルキノリンIr錯体Phq燐光分子
緑色発光： ベンゾチアヂアゾルBTの蛍光分子
青色発光： 発光分子基はフルオレンPFの蛍光分子

パワー効率１.9cd/A、最高輝度3585cd/m²

Copolymer	Bias [a] [V]	*J* [a] [mA cm^{-2}]	*LE* [a] [cd A^{-1}]	L_{max} [cd m^{-2}]	CIE [b] (*x*, *y*)
PFBT05-Phq2	6.8	2.5	2.8	2170	(0.34, 0.3
PFBT1-Phq2	6.7	5.6	1.9	3585	(0.34, 0.3
PFBT3-Phq2	7.4	5.2	1.8	2410	(0.32, 0.3
PFBT5-Phq2	6.3	2.2	6.1	10110	(0.32, 0.4
PFBT1-Phq1	6.4	3.4	3.6	6280	(0.26, 0.2
PFBT1-Phq4	6.0	3.1	4.7	5309	(0.38, 0.3
PFBT1-Phq5	5.9	1.5	5.6	6440	(0.44, 0.3
PFBT3-Phq3	6.4	2.3	4.6	6035	(0.31, 0.3

White light using color conversion method



Green (515 nm) phosphorescence emitter : $Ir(ppy)_3$

ITO/α-NPD/6.2mol% $Ir(ppy)_3$:TCTA/CF-X/Alq_3/LiF/Al

TCTA host; η_{ext}= **19.2 %** M. Ikai et al., APL **79** (2001)156.

Blue (465nm) phosphorescence emitter: Firpic

ITO/CuPc/α-NPD/6%FIrpic:host/BAlq/LiF/Al

CBP host; η_{ext}= **6.1**%, 7.7 lm/W

mCP host; η_{ext}= **7.5**%, 8.9 lm/W R.J. Holmes et al., APL **82**(2003)2422.

External quantum efficiency

$$\eta_{ext}(\%) = \gamma\, \eta_{ex}\, \eta_r\, \eta_{out}$$
$$= \eta_{int}\, \eta_{out}$$

γ : **carrier injection balance**

η_{ex} : **exciton formation efficiency**

η_r : **exciton recombination efficiency**

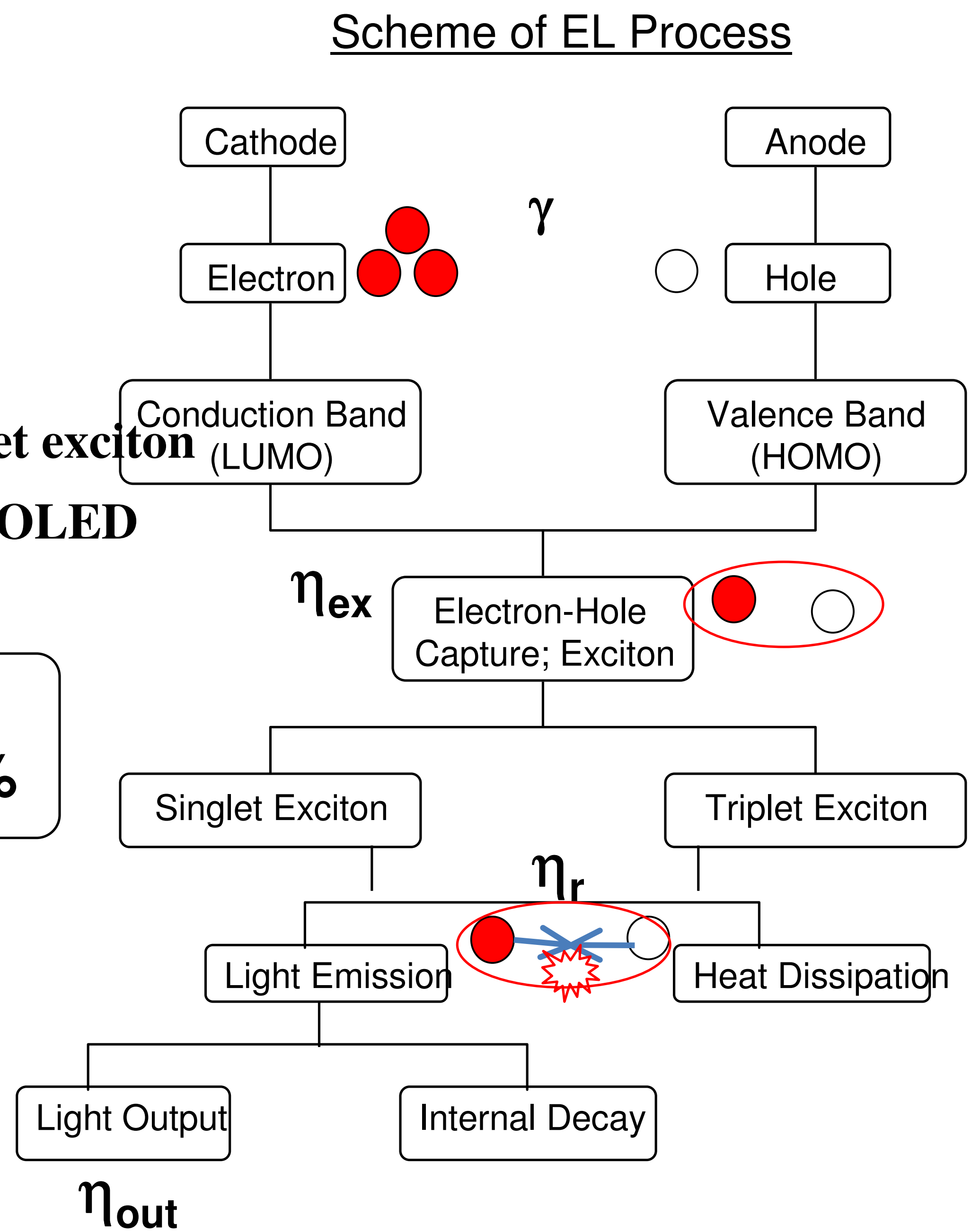
0.25 for singlet exciton, 1.0 for triplet exciton

η_{out} : **outcoupling effi. for light from OLED**

$\eta_{out} \sim 1/2n_a^2 \quad (=20\%)$

Phosphorescent emitters

$\eta_{int} = 100\%$, $\eta_{ext}(\%) = 20\ \%$



Host materials for blue emitters

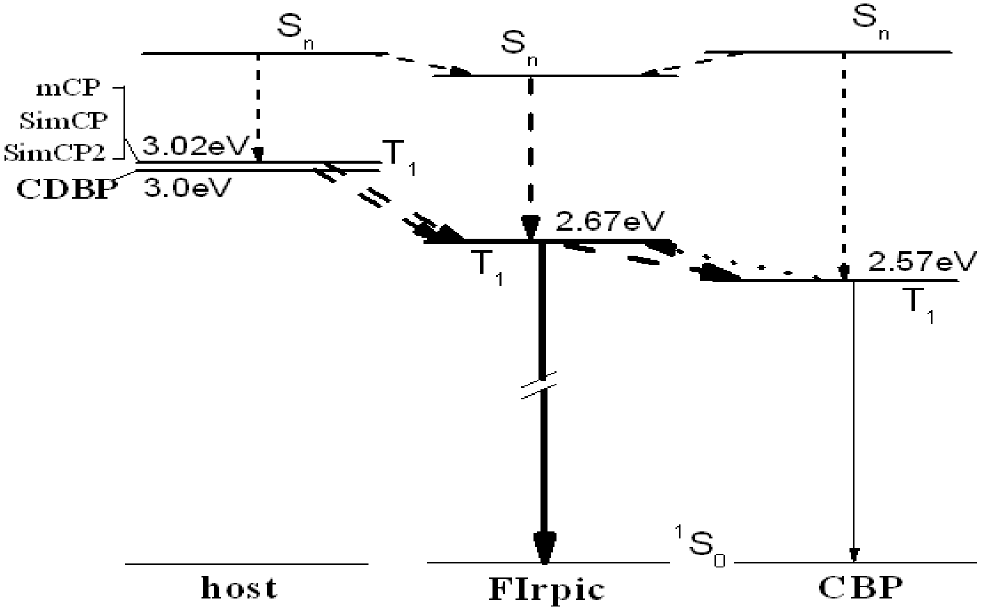
Currently very weak efficiency

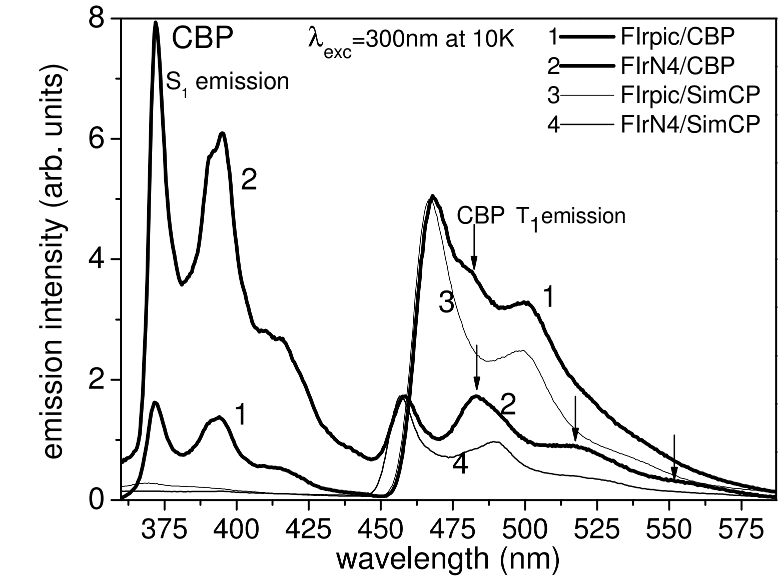
ITO/CuPc/α-NPD/6%FIrpic:host/BAlq/LiF/Al

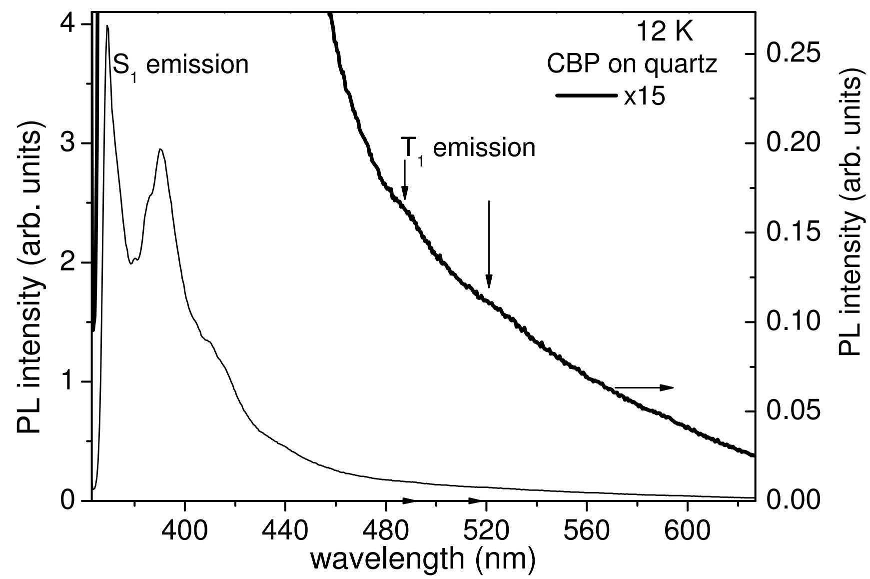
CBP: **6.1%**, 7.7 lm/W

mCP:**7.5**%, 8.9 lm/W

R.J. Holmes et al., *APL* **82**(2003)2422.

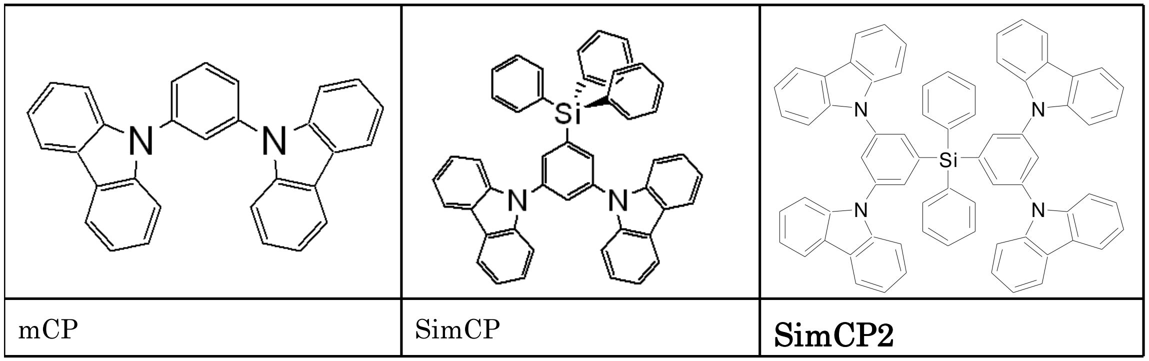




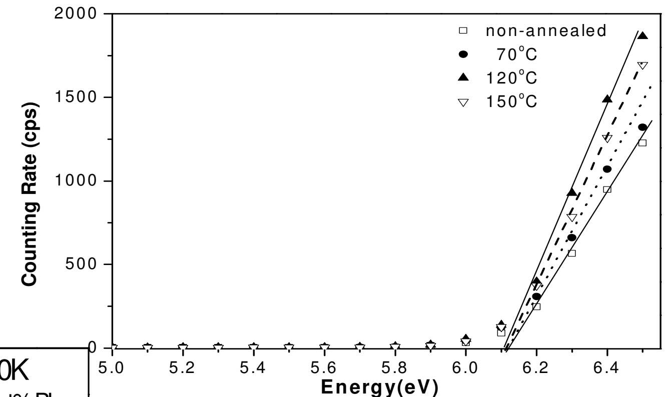


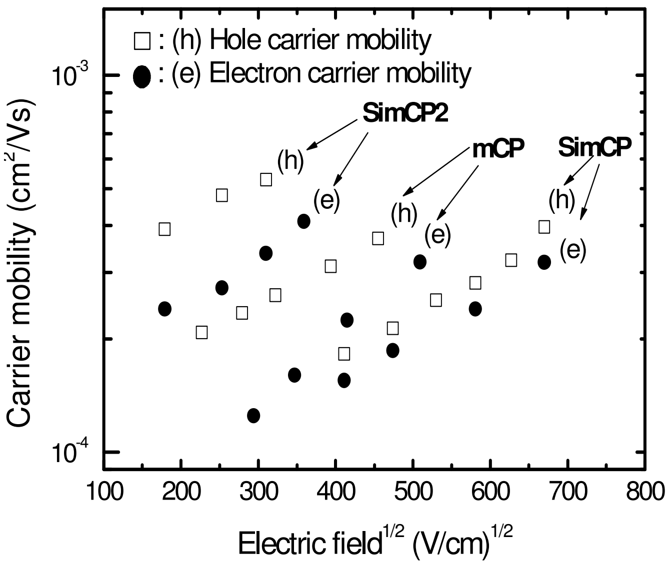
Highly stable (high glass transition temp.),
high carrier mobility,
high T_1 energy level hosts are necessary.

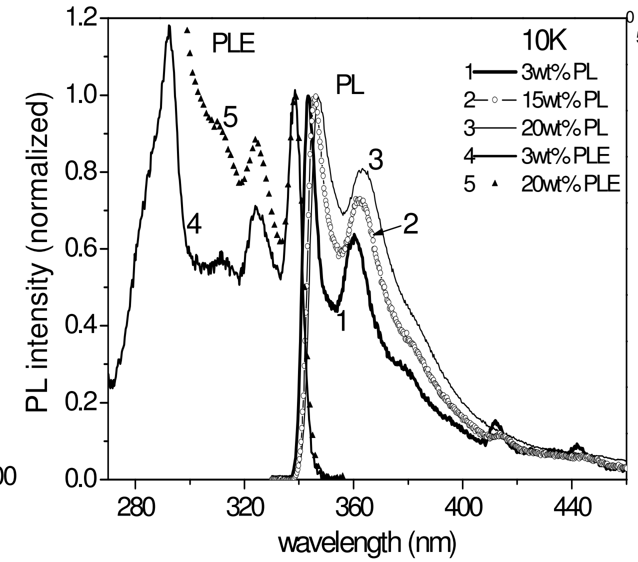
The best host material for blue emitter in OLEDS



bis(3,5-di(9H-carbazol-9-yl) phenyl)diphenylsilane (SimCP2)







SimCP2: Tg= 148 C

mCP: 55 C

SimCP: 101 C

CBP: 62 C

SimCP2 HOMO : 6.12 eV

LUMO : 2.56 eV,

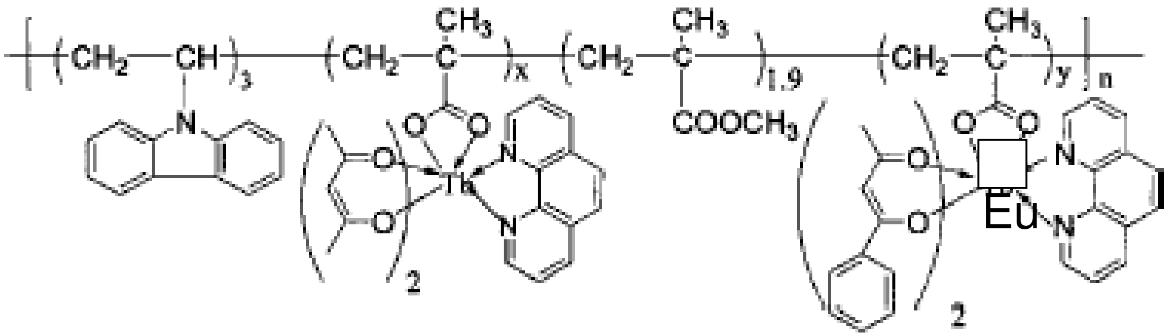
η_{ext} of **<u>17.7 %</u>** and power efficiency of **<u>24.2 lm/W</u>** at 100 cd/m² for FIrpic

ITO/PEDOT:PSS(35nm)/14 wt% FIrpic:SimCP2(35nm)/TPBi(28nm)/LiF/Al

c.f., 10.4 and 5.9 lm/W in the case of SimCP and mCP hosts, respectively

T. Tsuboi., M.-F. Wu, S.-W. Liu, C.-T. Chen, Org. Electron. (2009), in press.

Copolymer with Rare-earth-complex organic molecules

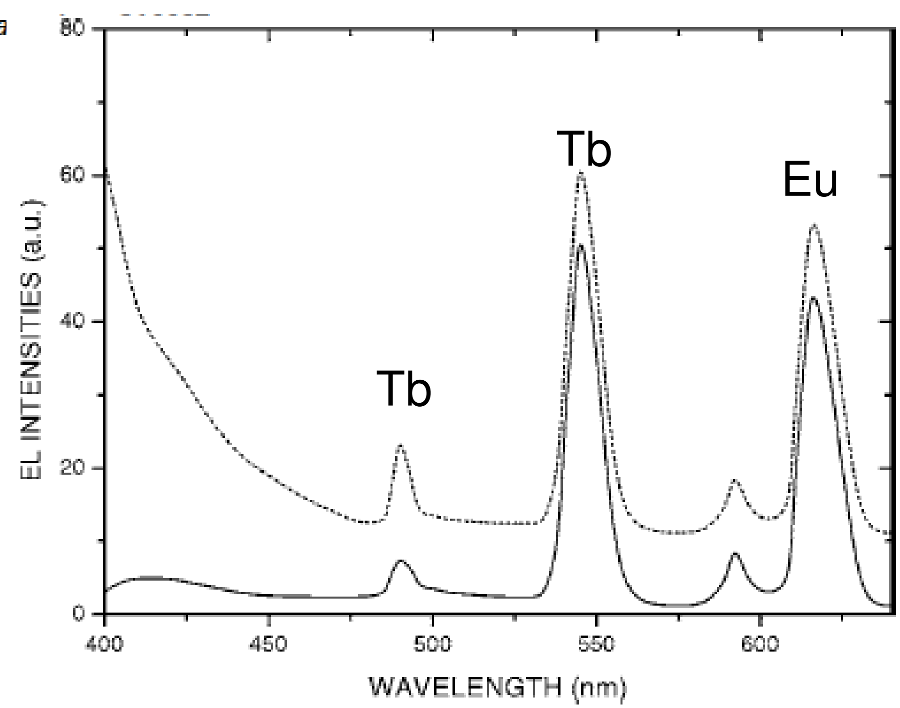


JOURNAL OF MATERIALS SCIENCE 39 (2004) 1407 – 1409

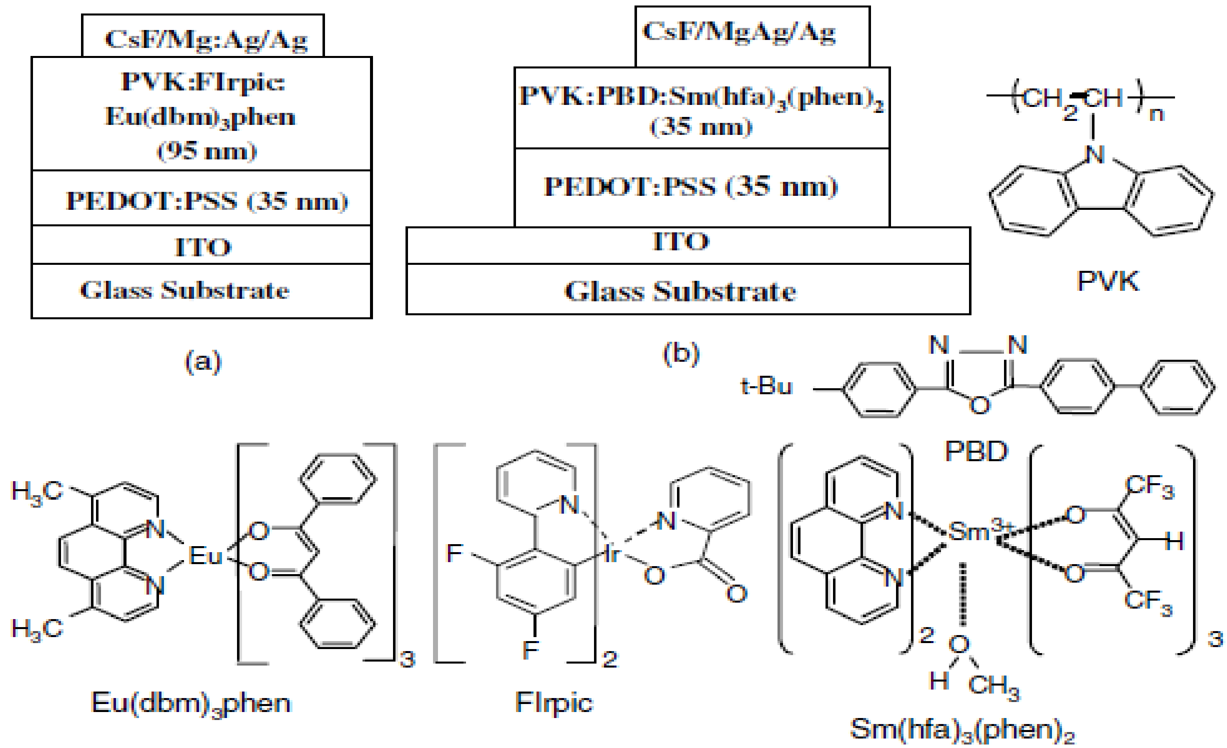
Novel ternary copolymer containing both Tb(III) and Eu(III) complexes for white-light electroluminescence

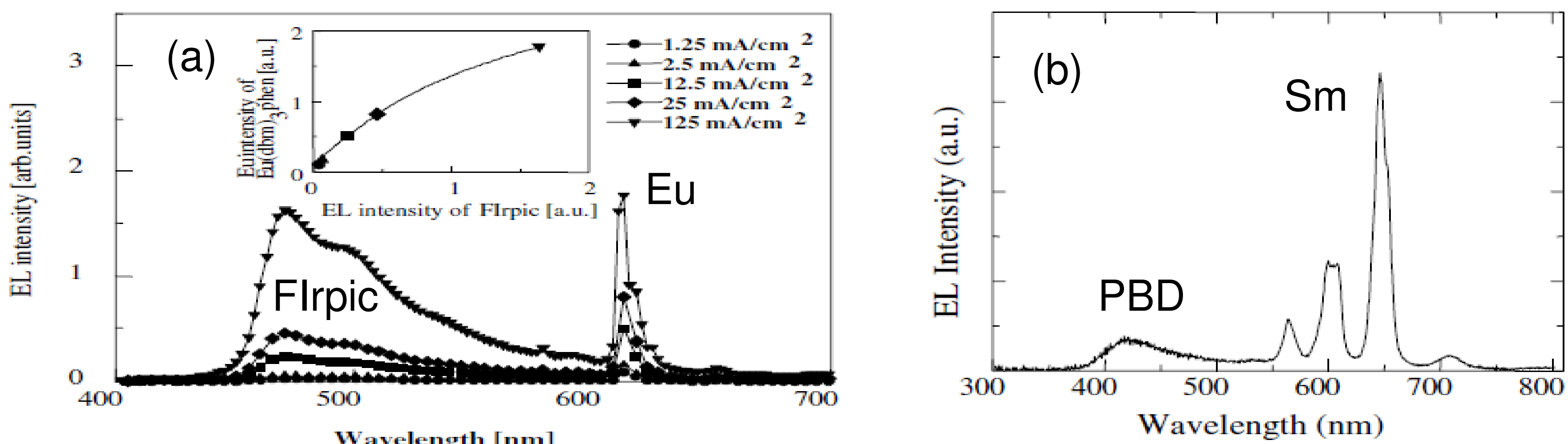
M. J. YANG, L. C. ZENG, Q. H. ZHANG
Department of Polymer Science and Engineering, Zhejiang University, Ha
People's Republic of China
E-mail: yangmj@cmsce.zju.edu.cn

high color purity with sharp lines



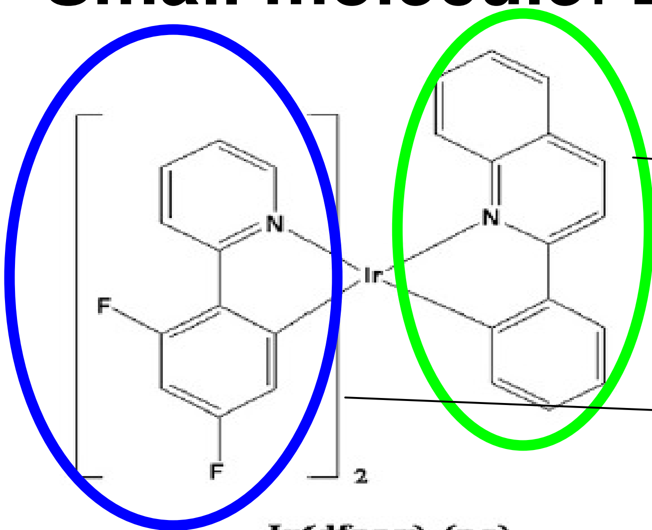
White OLED with rare-earth small molecules





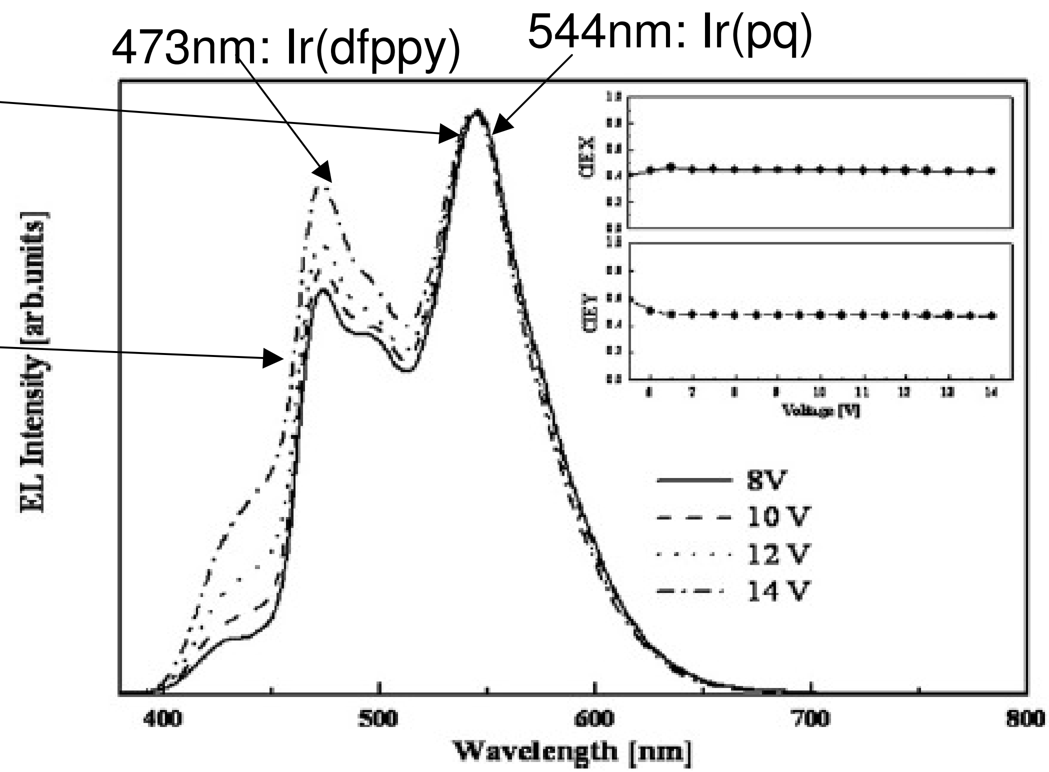
Z. Kin et al., Mater. Res. Soc. Symp. Proc. Vol. 965(2007) 0965-S04-02

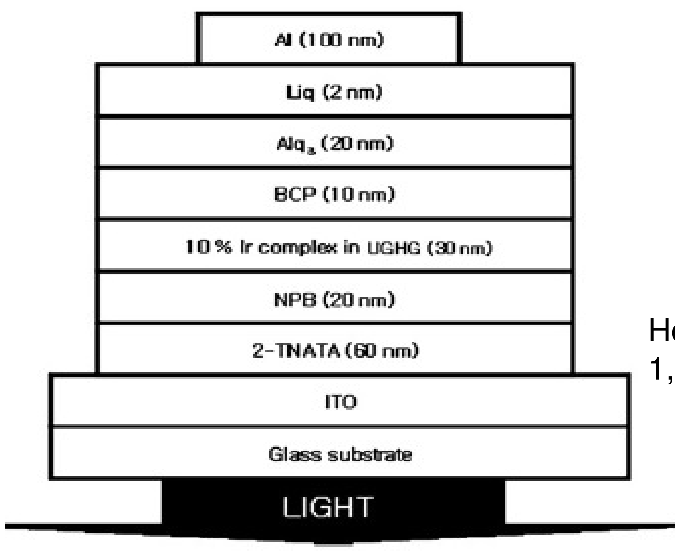
Small molecule: Dual emission from a single molecule



$Ir(dfppy)_2(pq)$

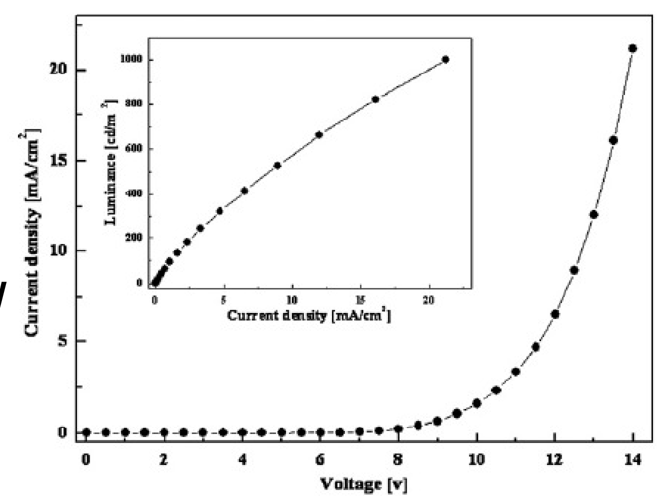
$Ir(dfppy)_2(acac)$: 469nm PL
$Ir(pq)_2(acac)$: 597nm PL





Host: UGH2
1,4-phenylenesis (triphenylsilane)

Max: 11.0 cd/m², 5.60 lm/W



J.H. Seo et al, Thin Solid Films 516(2008)3614.