

Vacuum Deposited Organic Light Emitting Devices on Flexible Substrates

"what a long, strange trip it's been"

Final Program Review
Princeton University

May 3, 2002

Vacuum Deposited Organic Light Emitting Devices on Flexible Substrates

Support: DARPA (F33615-94-1-1414)

Program Managers: Gurdial Saini & Darrel Hopper

Agent: Wright Patterson AFB

Dates: 6/13/94 - 4/30/02

Team:

Princeton University (S. Forrest)

HRL (K. Sayyah) - End Dec. 31, 00

Universal Display Corporation (J. J. Brown) - End Dec. 31, 00

University of Southern California (M. E. Thompson)

Program Objective

Demo PM & AM flexible displays by pushing the state of the art in OLED technology using SOLEDs, FOLEDs, OVPD, lasers and organic transistors.

Team Responsibilities

- **Princeton:** Develop flexible, transparent, stacked and ultrahigh efficiency OLEDs and packaged display pixel arrays. Initial reliability testing. Organic transistors and roll-to-roll processing demonstrations.
- **USC:** Organic materials development for high reliability, efficient, saturated color.
- **HRL:** Si TFT AM development on glass and flexible substrates using lift-off. Qualification for DoD and civilian applications.
- **UDC:** Reliability studies of AM & PM flexible displays. Display manufacturing development and scale-up. Formation of strategic alliances.

Specific Objectives

- Demo. flexible, ultralight weight, AM displays. (x)
- Demo. RGB SOLED pixel with true color (✓)
- Demo. high efficiency OLEDs with luminescence in the R, G & B using vacuum-deposited organics (✓)
- Demo. scalability to large substrates (✓)
- Demo. photolith patterning of high resolution pixels (✓)
- Demo. OLED reliability (✓)
- Demo. organic-TFTs for displays
- Develop methods to select optimal materials for high efficiency displays (✓)
- Refine processes for prototype and manufacture (✓)

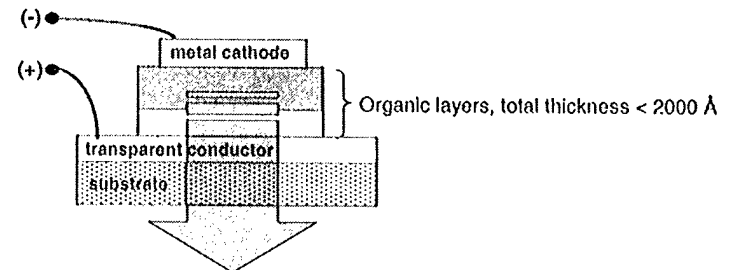
Accomplishments

- Demo'd transparent, true color patterned SOLEDs
 - ✓ Developed full, *quantitative* understanding of microcavity effects
- Demo'd efficient R, G, B color emission
 - ✓ Demo'd electrophosphorescent efficiencies in red and green (19%, int. eff. ~87%)
 - ✓ Demo'd phosphor-sensitized fluorescence with efficiencies of 8%.
 - ✓ Extremely long operational lifetimes found for some phosphors
- Demo'd efficient TOLEDs for head-up, integrated apps.
- Tech. transfer to UDC (facility on line) & HRL
- Demonstrated method for micropatterning of displays: cold-welding followed by lift-off
- Demonstrated growth of OLEDs via OVPD
 - ✓ Equipment manufacturer building large scale production tools

Technology Transfer

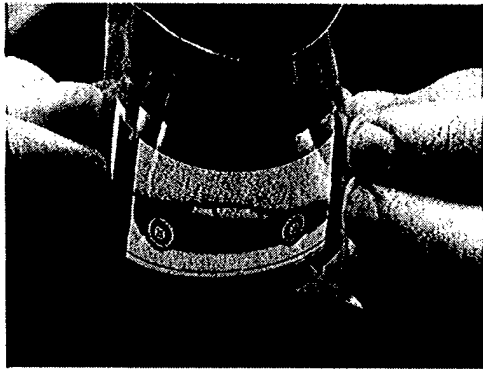
- ~40 Patents pending
 - ✓ Architectures, materials, packages, phosphorescence, transistors, patterning
 - ✓ ~50 issued: FOLED, TOLED and SOLED parent case, phosphorescence, patterning, laser, vacuum and OVPD deposition basic patents.
 - ✓ All patents filed globally, with exclusive rights to UDC.
- Established strong ties with potential manufacturers of equipment and panels
- Prototyping and Tech. Transfer facility opened by Universal Display- Significant resource leveraging and customer interest

Benefits of OLEDs



- can be prepared on any substrate - active materials are amorphous

Flexible, Passive Matrix OLED Display



Courtesy: Universal Display Corp.

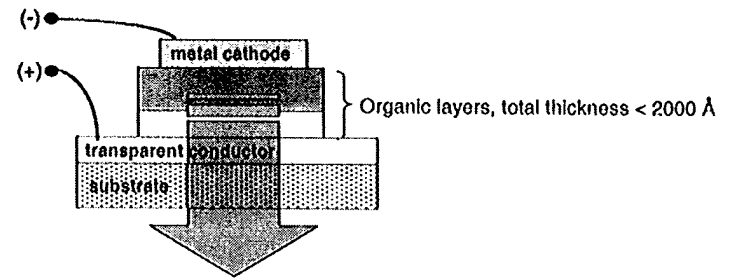
Flexibility is a transformational advantage of OLEDs.

But significant challenges remain:

- Lifetime must improve
- Conformal vs flexible
- Mechanical ruggedness

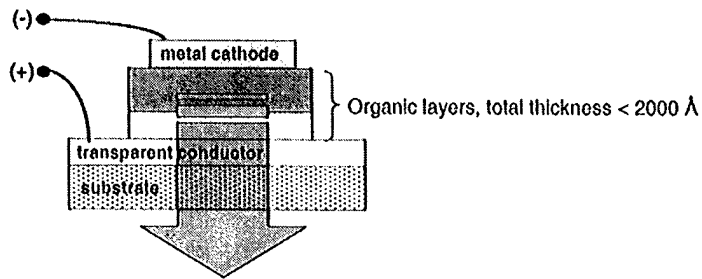
128x64 pixels, 400x500µm each
 Display dimension: 2"x3"
 Full motion video

Benefits of OLEDs



- low cost materials and fabrication methods, scalable to large area

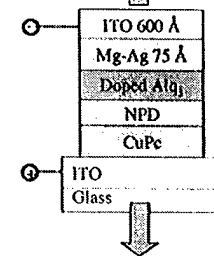
Benefits of OLEDs



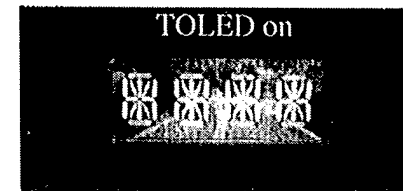
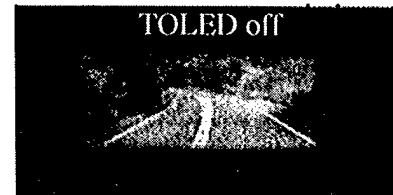
- readily tuned color and electronic properties via Chemistry
- can be transparent when off

Transparent OLEDs (TOLEDs)

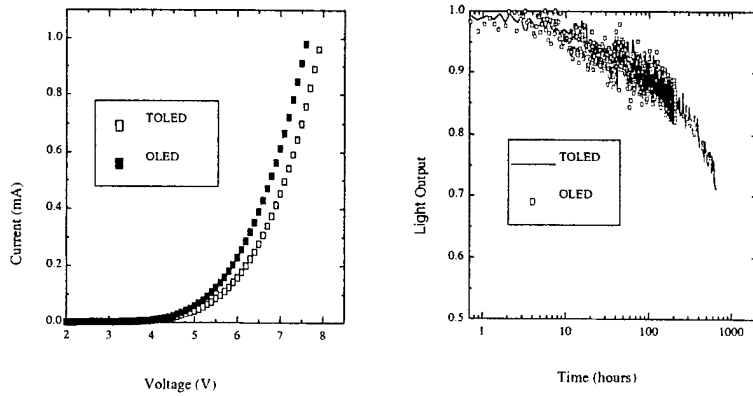
- Devices can be > 90% transparent
- Thin metal or electron injection layer is capped with ITO
- Transparent cathode can also be used



Bulovic et al., Nature 1996



TOLED Current-Voltage and Lifetime Characteristics



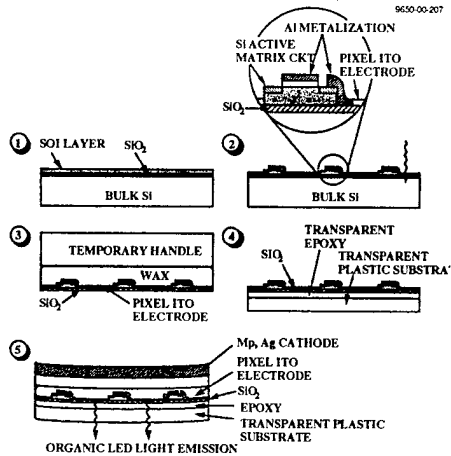
Sony 13 inch AMOLED-TFT Display



800x600 pixels
Full Color
Top emission

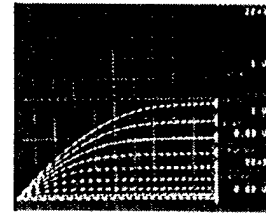


Schematic of Flexible AM-OLED Fabrication Process



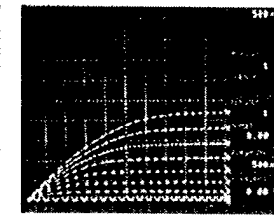
Characterization of Bonded-SOI PMOS Transistors (2)

PMOS Bonded-SOI I-V Characteristics



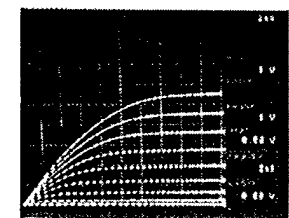
$L_G = 10 \mu\text{m}; W_G = 5 \mu\text{m}$

$I_{SD} = 97 \mu\text{A}$
 $V_{SD} = 10 \text{ V}$
 $V_{SG} = 10 \text{ V}$



$L_G = 10 \mu\text{m}; W_G = 100 \mu\text{m}$

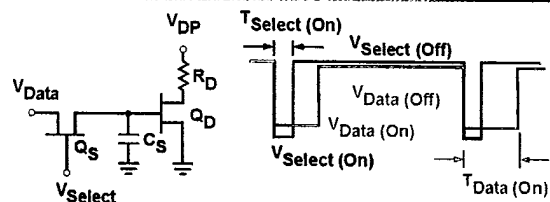
$I_{SD} = 2.2 \text{ mA}$
 $V_{SD} = 10 \text{ V}$
 $V_{SG} = 10 \text{ V}$



$L_G = 10 \mu\text{m}; W_G = 500 \mu\text{m}$

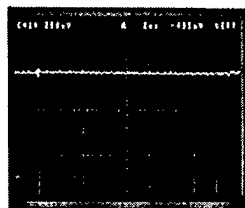
$I_{SD} = 11.0 \text{ mA}$
 $V_{SD} = 10 \text{ V}$
 $V_{SG} = 10 \text{ V}$

Characterization of Bonded-SOI Two Transistor Active Matrix Circuit (Resistor Load)

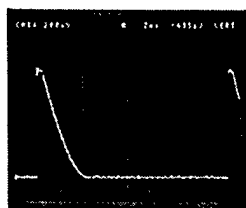


Wafer	C_S [pF]	$\Delta I_L / I_L(O)$
A-1	0.5	2%
A-1	1.1	<1%
A-1	11.0	<0.5%
A-2	0.5	<1%
A-2	1.1	<1%
A-2	11.0	<0.5%
A-3	0.5	2%
A-3	1.0	<0.5%
A-3	11.0	<0.5%
A-4	0.5	3%
A-4	1.1	2%
A-4	11.0	<0.5%
A-5	0.5	<0.5%
A-5	1.1	<0.5%

$V_{Select (On)} = -12 V$ $C_S = 0.5 pF$ $V_{Data (On)} = -10 V$
 $T_{Select (On)} = 100 \mu s$ $T_{Frame} = 16 ms$ $T_{Data (On)} = 500 \mu s$

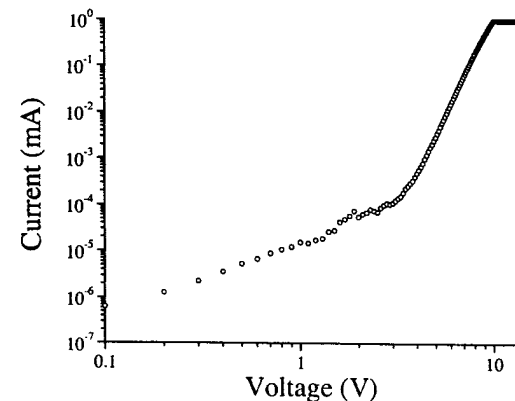


$V_{Select (Off)} = 0 V$



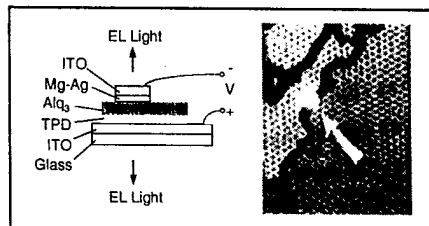
$V_{Select (Off)} = -1.6 V$

Data Summary for TOLEDs on Hughes Si

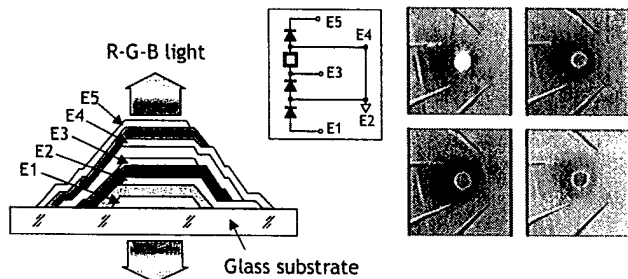


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Transparent & Stacked Organic Light Emitting Devices for Full Color Generation

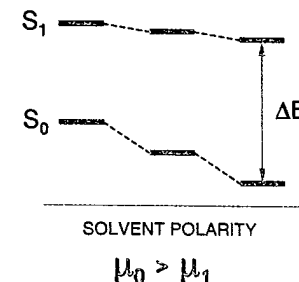
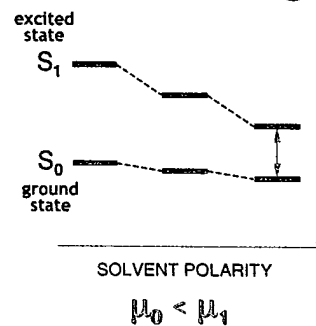
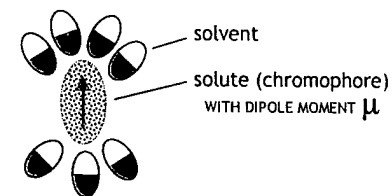


V. Bulovic, et al, *Nature*, 380 29 (1996)



G. Parthasarathy, et al., *Adv. Mater.*, 11, 907 (1999).

Influence of μ_0 and μ_1 on Chromatic Shift Direction



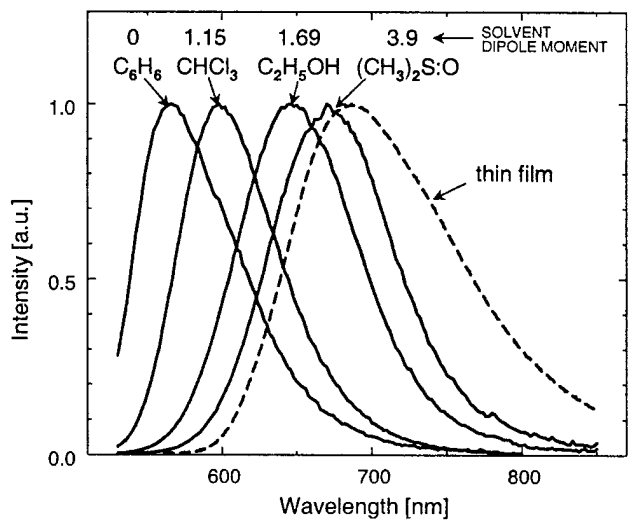
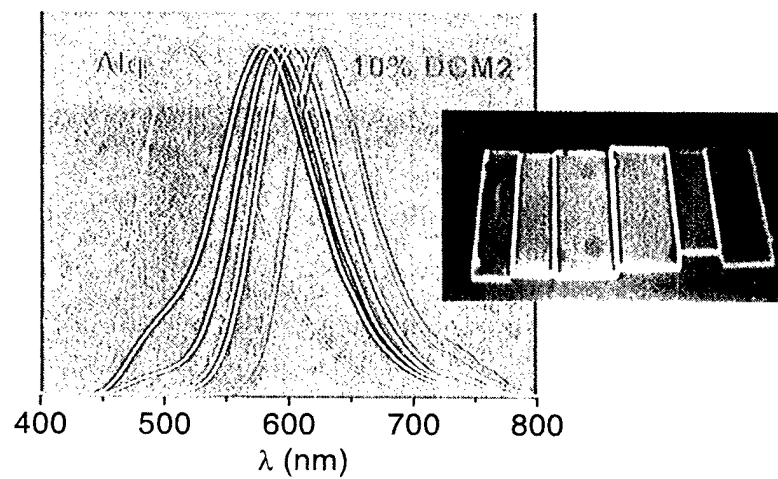


Figure 3, Bulovic et al.



Peak EL of DCM2 in Different Hosts

Bulovic et al., *Chem. Phys. Lett.* submitted (1999).

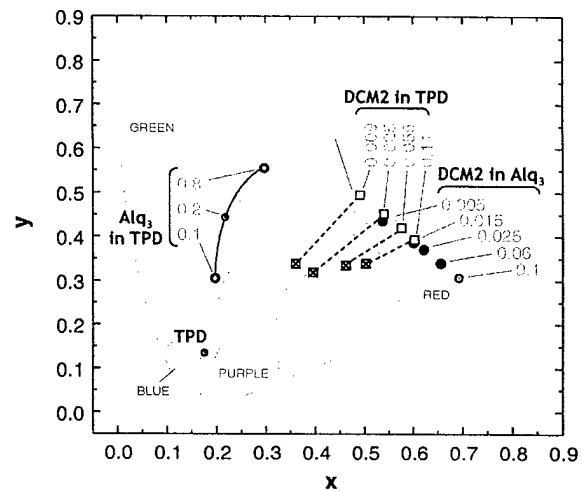
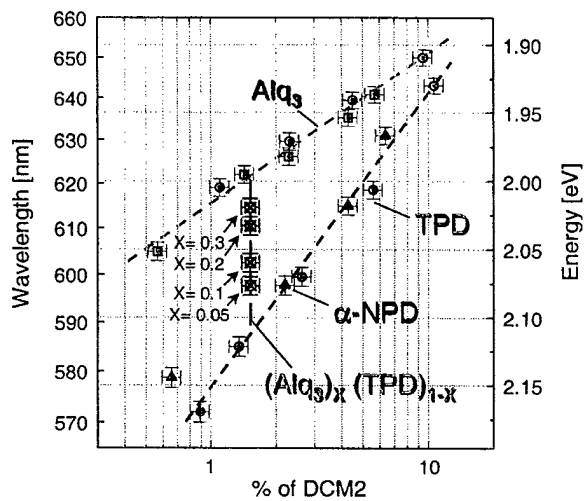
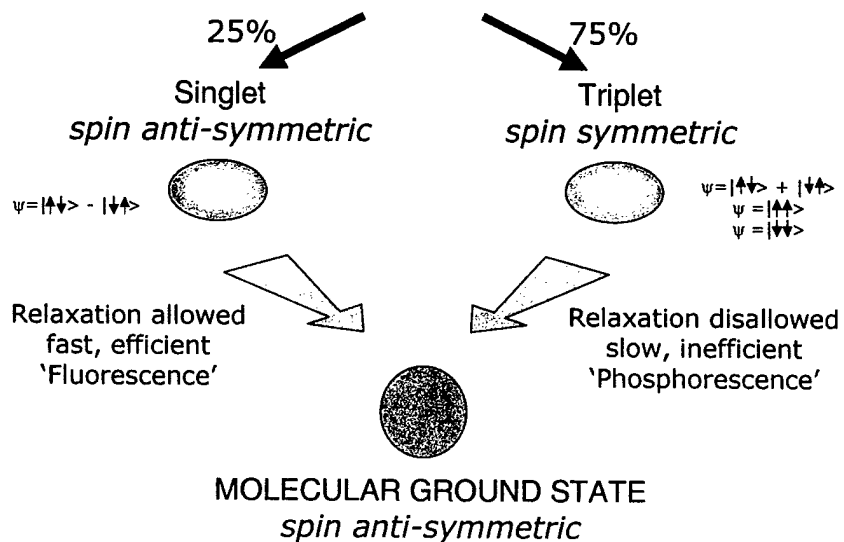
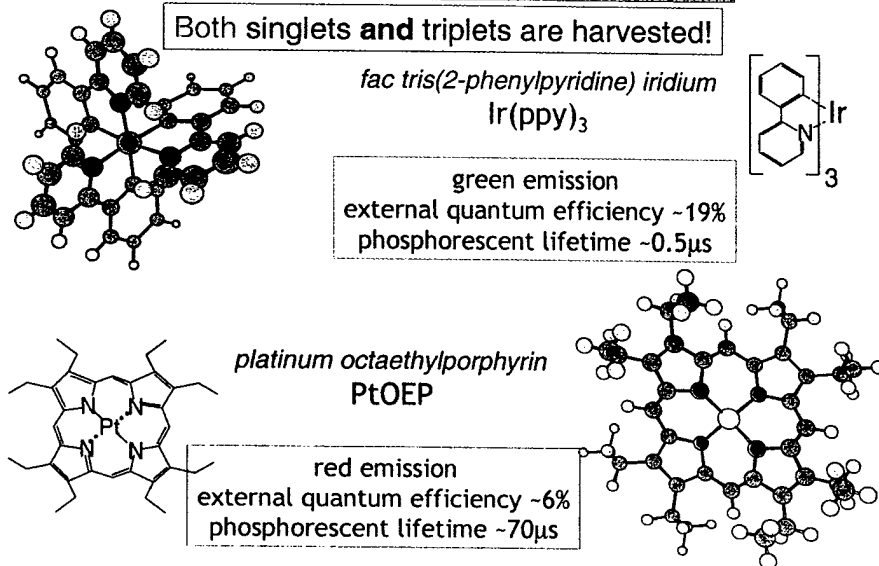


Figure 9, Bulovic et al.

MOLECULAR EXCITED STATES AFTER ELECTRICAL EXCITATION

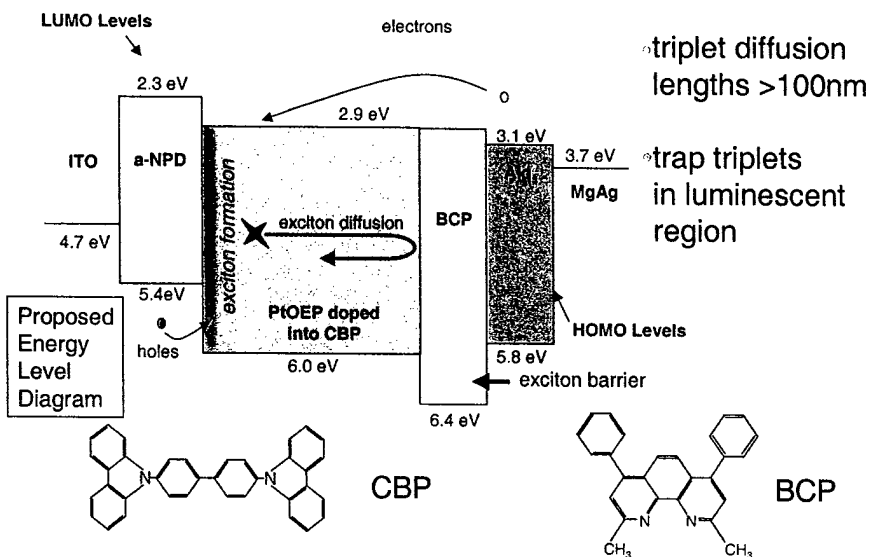


Phosphorescence enhanced by mixing the singlet and triplet excited states eg: spin orbit coupling via heavy metal atom (Pt or Ir)



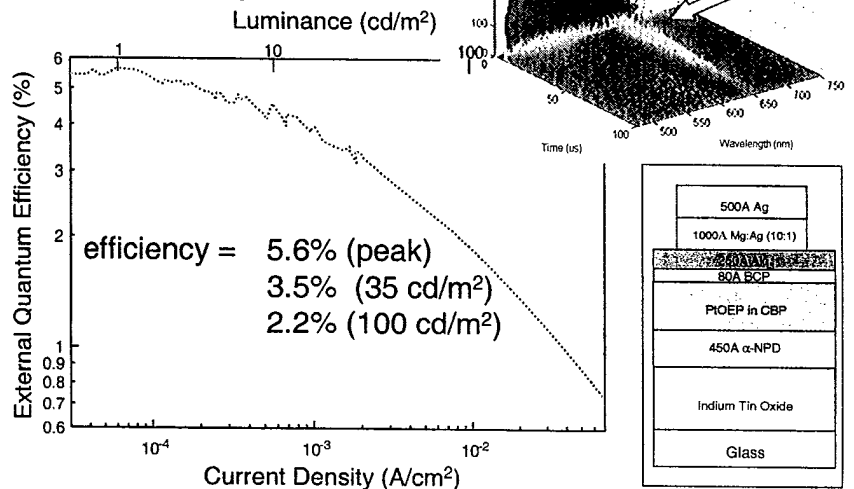
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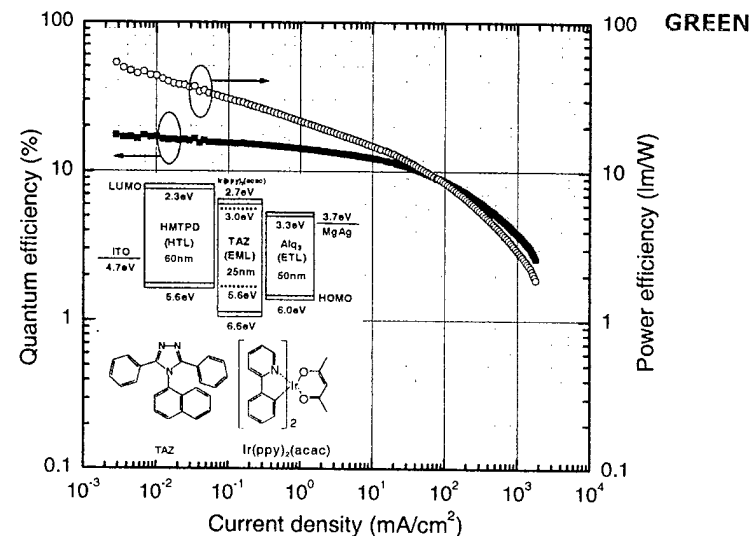
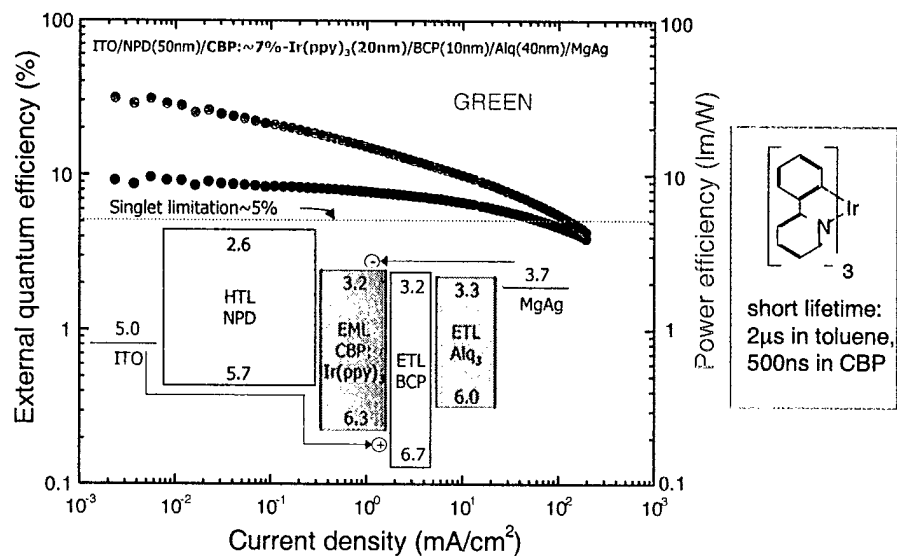
Electrophosphorescent device structure



6% PtOEP in CBP

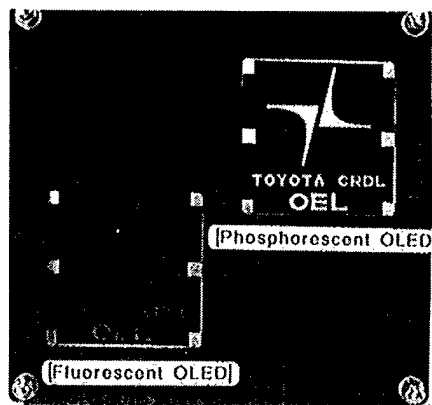
- Exciton blocker increases eff. by 50%
- Roll off at modest luminance levels
- Transfer by trapping





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OLED panels of fluorescence and phosphorescence



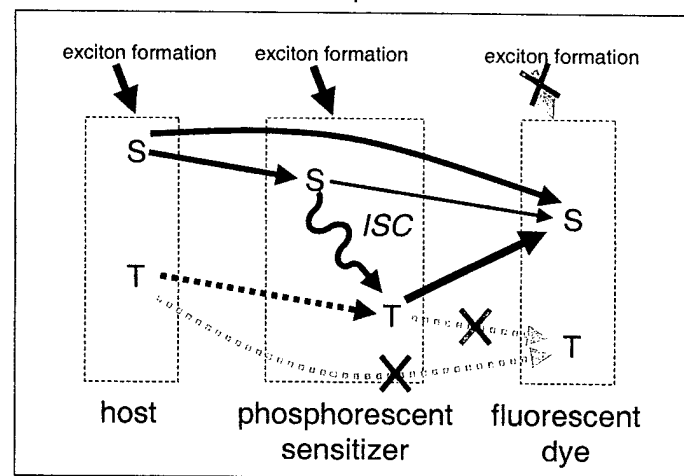
Conventional OLED Phosphorescent OLED

2001 MRS spring meeting, San Francisco, Paper C4.3

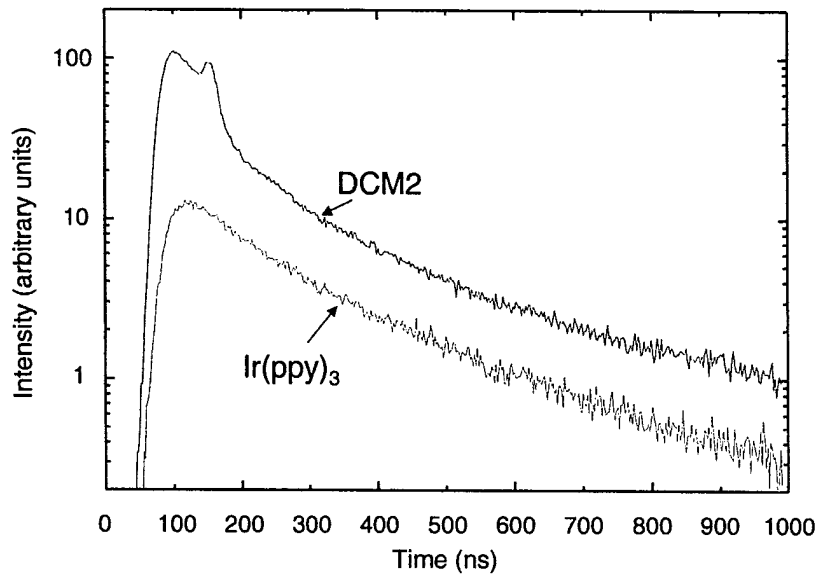
TOYOTA CENTRAL R&D LABS., INC.

TRIPLET-SINGLET TRANSFER

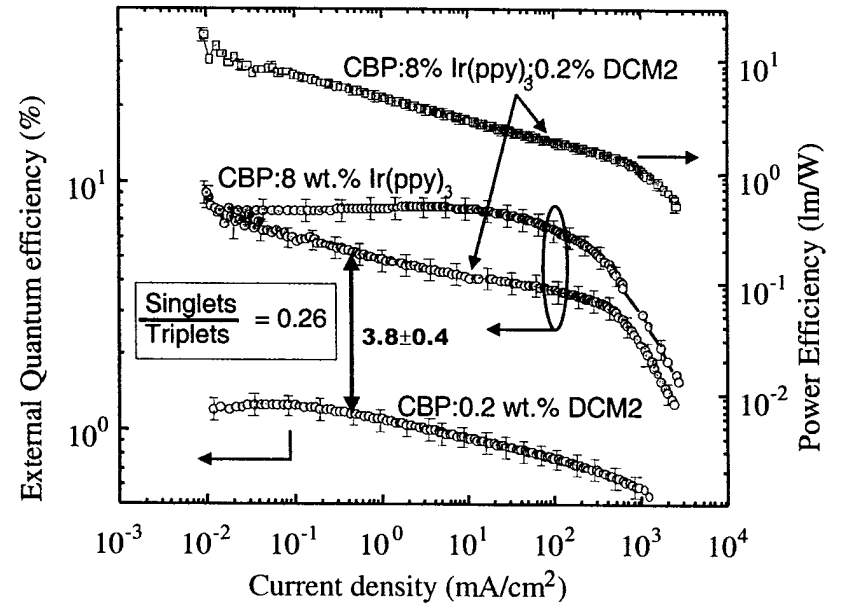
- ◇ Need separation between phosphorescent donor and fluorescent acceptor to prevent direct Dexter transfer to fluorescent triplet state
- ◇ Transfer possible for radiative triplet states



OLED Transient Response

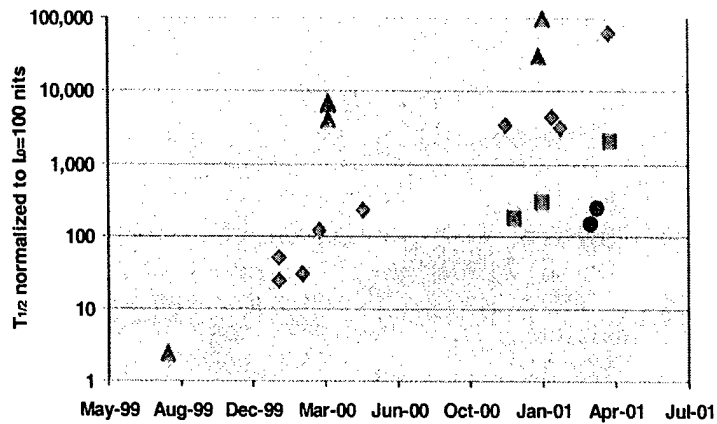


◇ Delayed DCM2 fluorescence confirms sensitizing action of Ir(ppy)₃



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Phosphorescent OLED Lifetime



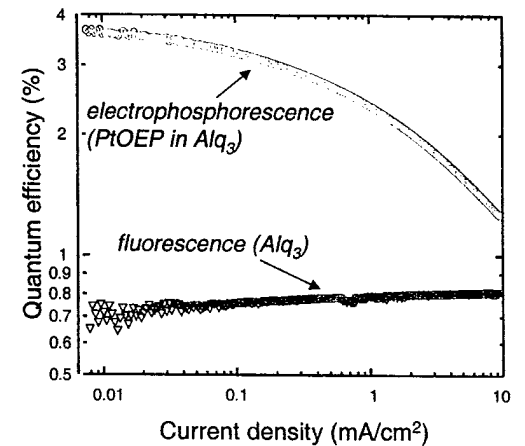
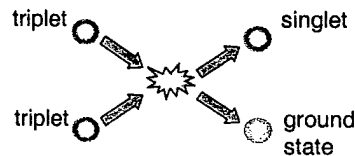
UNIVERSAL DISPLAY CORPORATION

PHOSPHORESCENT EFFICIENCY DEGRADES WITH CURRENT DENSITY

Is it saturation of phosphorescent sites?

Current densities too low. Should be proportional to $1/J$ but actually closer to $1/\sqrt{J}$.

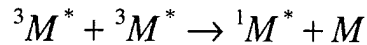
Or T-T annihilation?



Can the degradation be minimized?

THEORY

T-T annihilation destroys two triplets and creates a singlet



Transient model:
$$d[{}^3M^*] = -\frac{[{}^3M^*]}{\tau} - k_q[{}^3M^*]^2 + \frac{J}{qd}$$

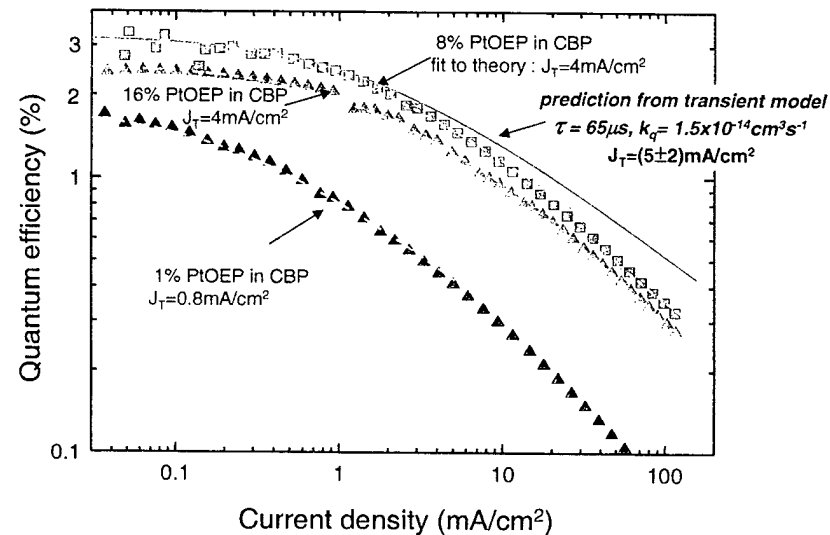
τ : triplet lifetime	J : current density
k_q : T-T annihilation rate	d : thickness of active layer

Transient solution:
$$[{}^3M^*(t)] = \frac{[{}^3M^*(0)]}{(1 + [{}^3M^*(0)]\tau k_q) e^{t/\tau} - [{}^3M^*(0)]\tau k_q}$$

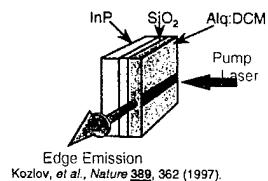
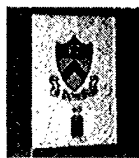
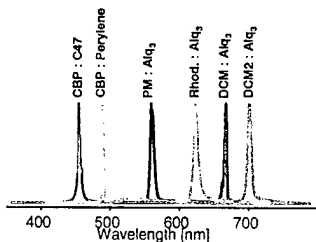
Steady state solution:
$$\frac{\eta}{\eta_0} = \frac{J_T}{4J} \left(\sqrt{1 + 8 \frac{J}{J_T}} - 1 \right) \quad \begin{array}{l} \eta: \text{quantum efficiency} \\ \eta_0: \text{max efficiency} \end{array}$$

Threshold current density:
$$J_T = \frac{2qd}{k_q \tau^2} \quad (\text{for } \eta = \eta_0/2)$$

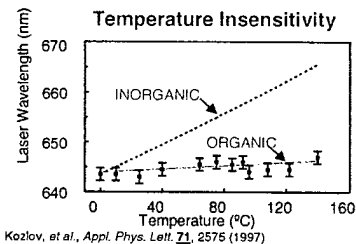
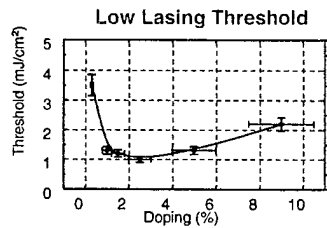
PREDICTION FROM TRANSIENT MODEL MATCHES MEASUREMENT



Organic Lasers

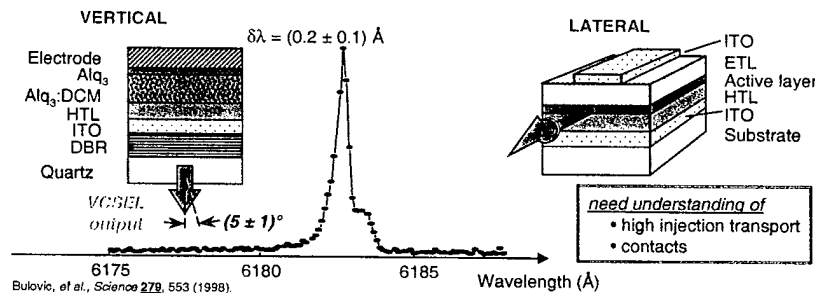


- Motivation**
- Material Tunability
 - Freedom from Epitaxial Limitations
 - Natural Quantum Dots

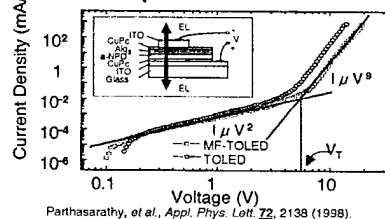


Organic Lasers

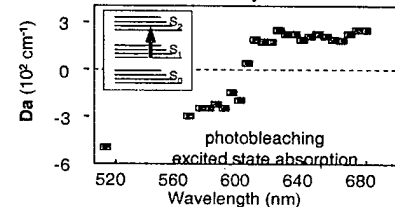
Electrically Pumped Structures



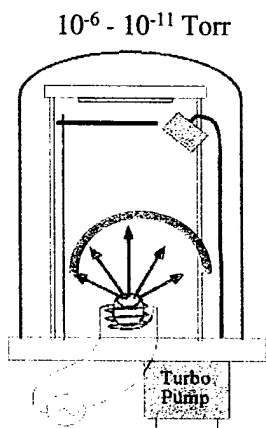
Transparent Contacts



Electrical Pump - Optical Probe



Vacuum Deposition



Advantages

- Simple
- Precise (monolayer) thickness control

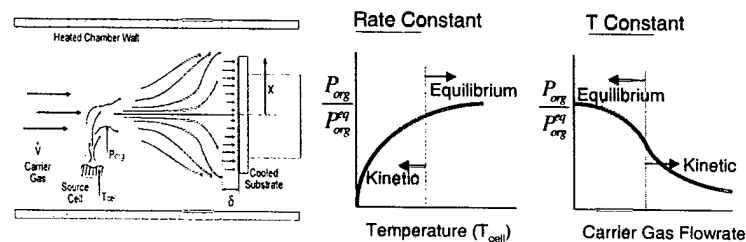
Disadvantages

- Inefficient use of material
- Difficult to control dopant concentration
- Uneven deposition rate
- Chamber contamination and dust

→ Difficult to scale-up throughput

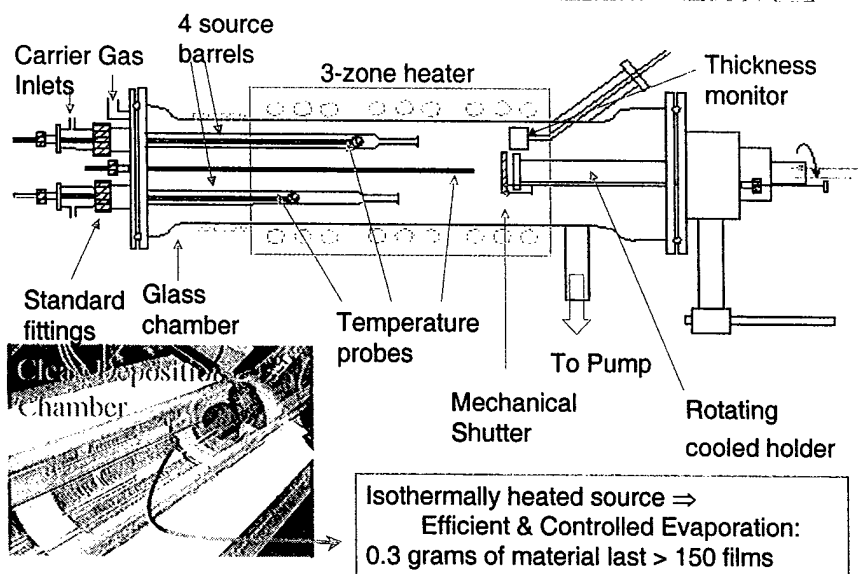
Organic Vapor Phase Deposition

Chamber pressure: 0.1-10 Torr

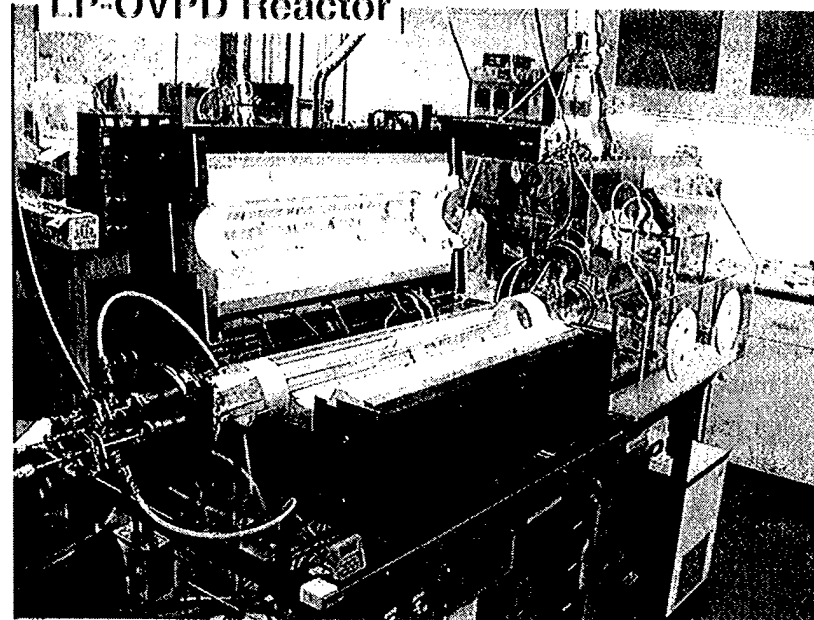


- Controlled and accurate doping
- Dust free chamber
- Efficient materials use
- Control of film crystal structure

OVPD: Deposition System Design

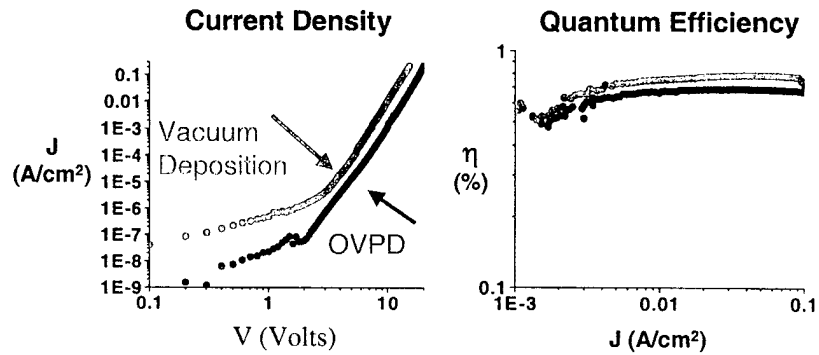


LP-OVPD Reactor

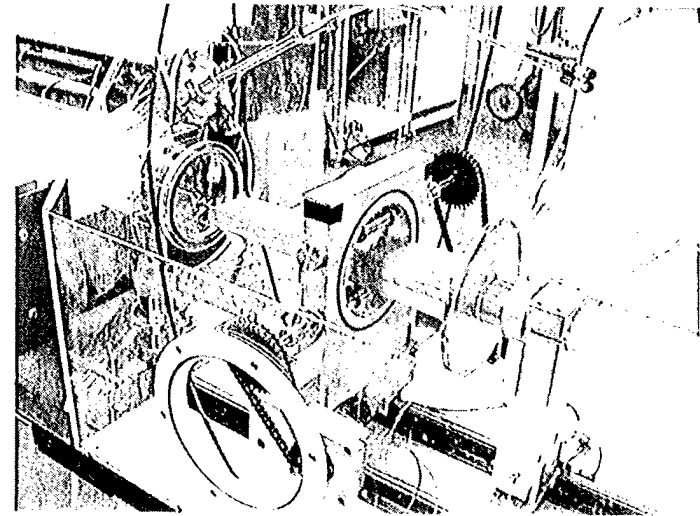


OVPD vs. Vacuum Deposition: OLEDs

MgAg	1000 Å
Alq ₃	500 Å
α-NPD	500 Å
ITO	1000 Å
Glass/Plastic	1 mm

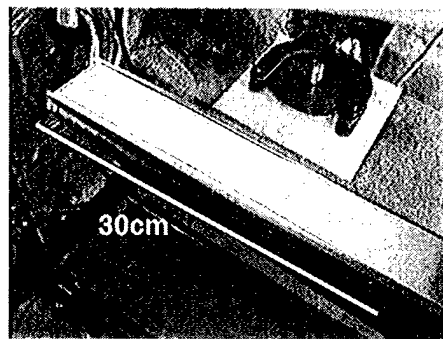


OVPD for Roll-to-Roll Deposition:



OVPD for Roll-to-Roll Deposition of OLEDs:

1st demonstrated OLED heterostructure and working device on >30 cm plastic ribbon

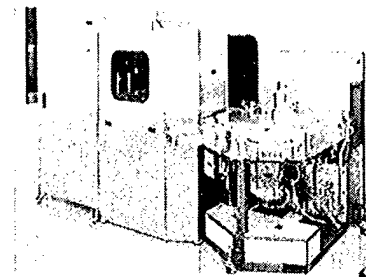


30x5cm, TPD/Alq₃ plastic ribbon substrate



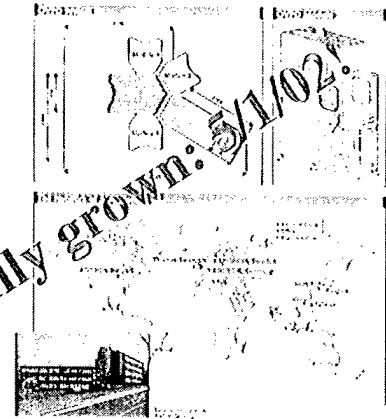
100x5cm, TPD/DCM2-Alq₃ plastic ribbon substrate

OVPD Equipment for OLEDs



Organic Vapor Phase Deposition

- Excellent uniformity
- High throughput
- Low cost
- High resolution
- High purity
- High efficiency
- High stability
- High reliability
- High yield
- High quality
- High performance
- High productivity
- High efficiency
- High stability
- High reliability
- High yield
- High quality
- High performance
- High productivity



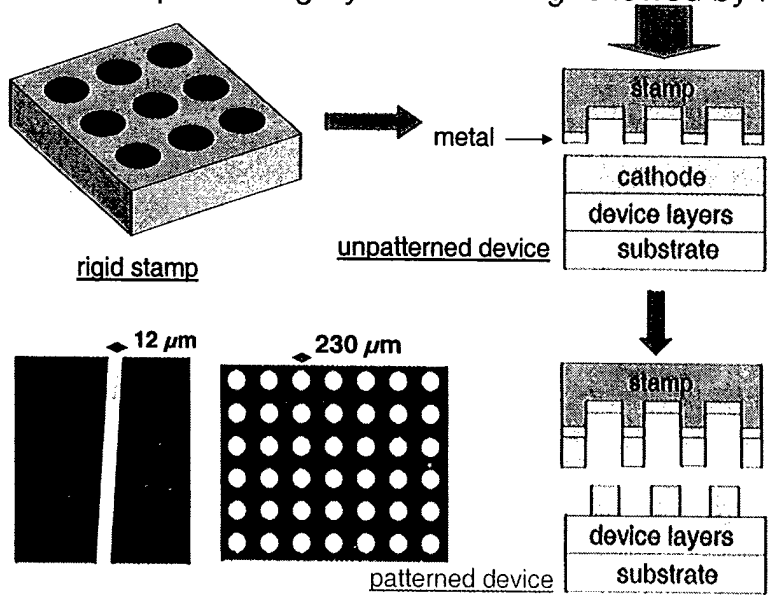
OLEDs successfully grown: 5/1/02!

AIXTRON

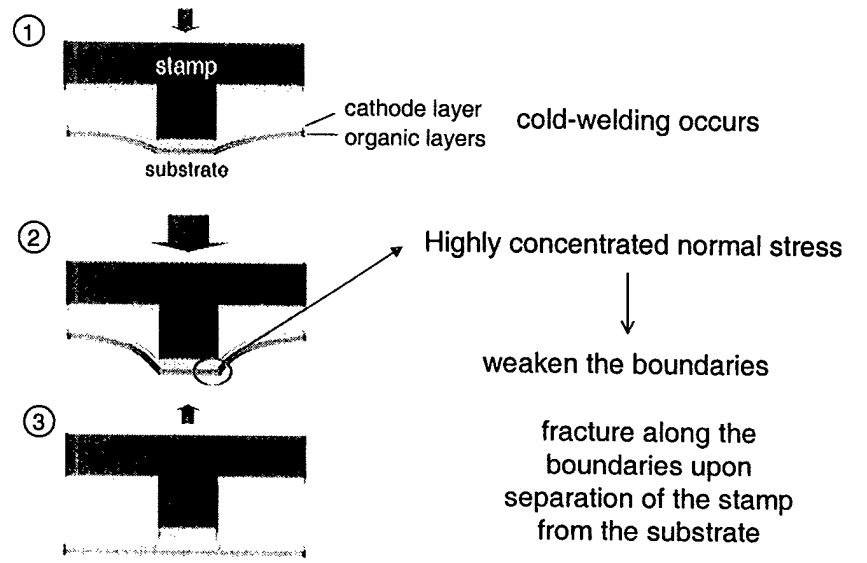
AIXTRON

... ..

Direct nanopatterning by cold-welding followed by lift-off

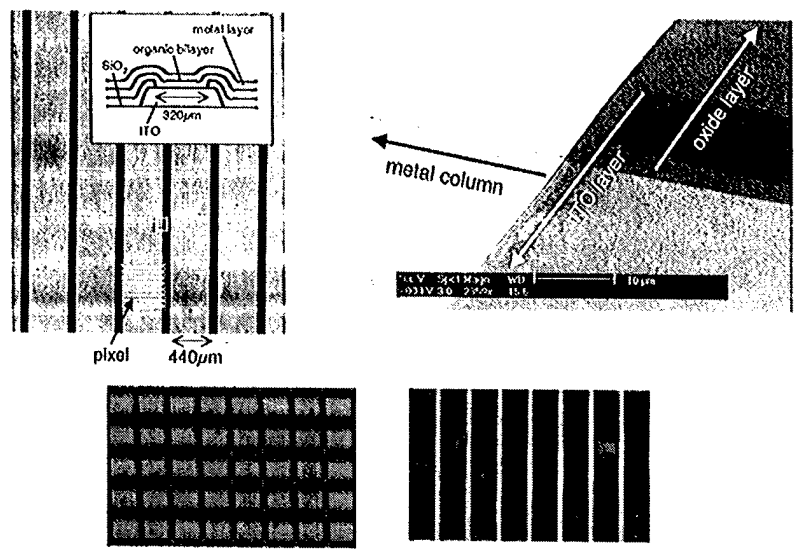


mechanism

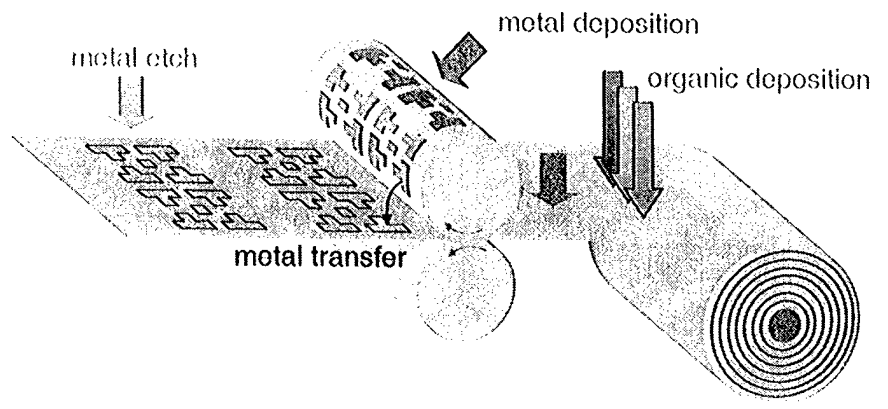


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Display Fabrication Using Cold-Welding Followed by Lift-Off



OVPD & Cold-Welding: web-processing of organic devices



Passive-Matrix OLED Display in Operation

Recent advances in small molecular weight displays

Stephen Forrest
 Department of Electrical Engineering
 Princeton University

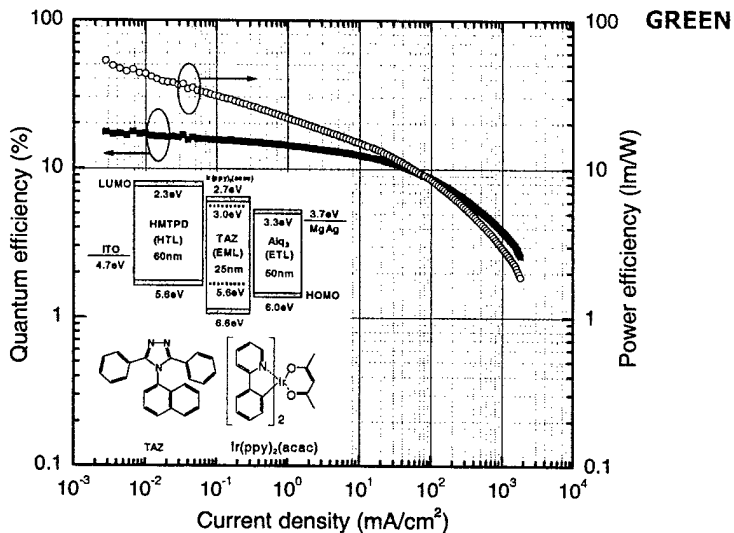
Princeton University

Accomplishments

- Achieved high brightness greens and deep blues
- Demonstrated efficient phosphor polymer devices
- Demonstrated efficient, simplified white OLEDs
- Modeled and demonstrated high resolution patterning by OVPD
- Developed "unified model" of current-voltage characteristics of OLEDs
- Demonstrated cold-welding by metal addition

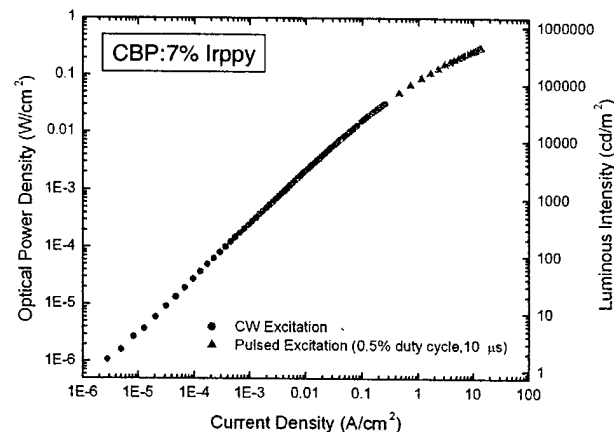
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Ir(ppy)₂(acac) doped ETL (Triazole) ($\eta_{ext}=19\%$, $\eta_{int}=87\%$)



Princeton University

High Brightness Phosphorescent Devices

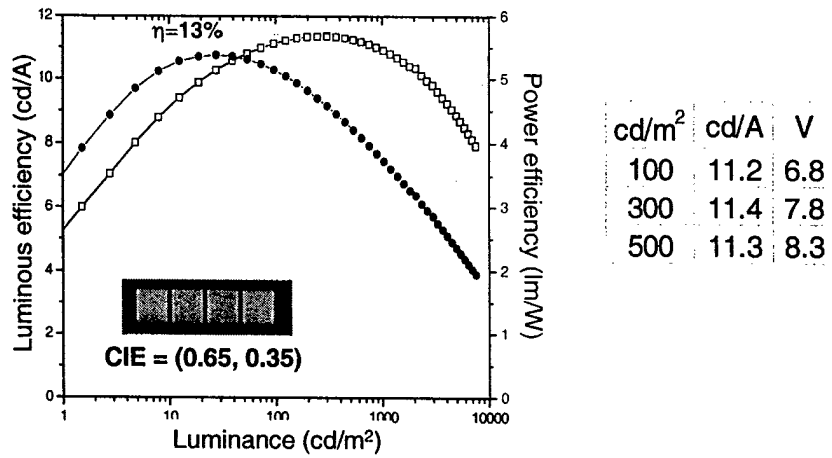


Peak brightness of a 13% efficient CBP:7% Irppy device approaches 5×10^5 cd/m² and 0.3 W/cm²

Compare to a 1.7% efficient CBP device with 6×10^4 cd/m² and an optical power density of 0.2 W/cm² under the same excitation

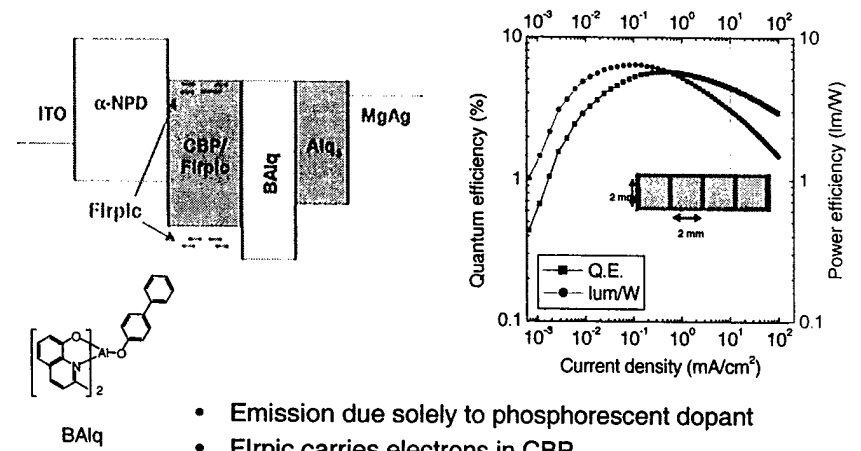
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Red PHOLED Performance



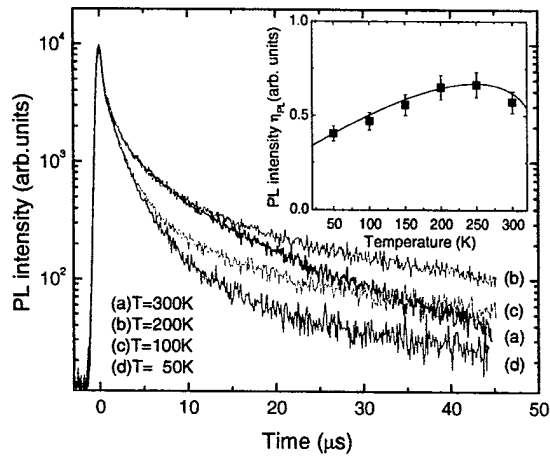
UNIVERSAL DISPLAY CORPORATION

Blue Electrophosphorescence from Flrpic/CBP



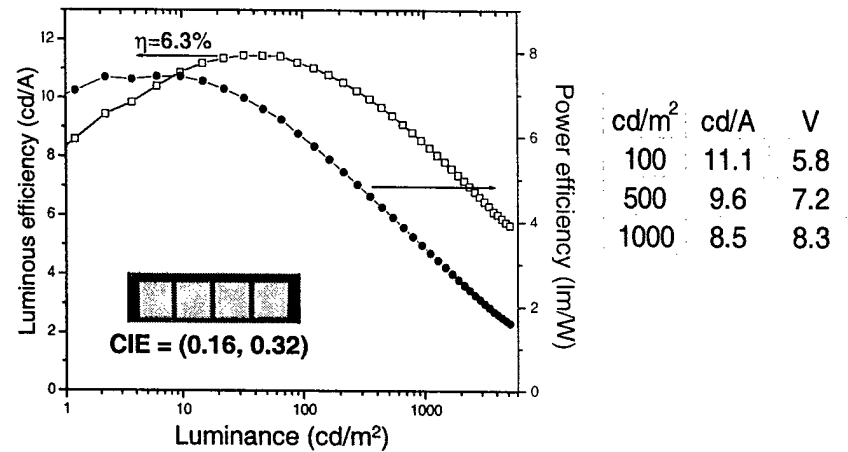
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Temperature Dependent PL of Flr(pic)



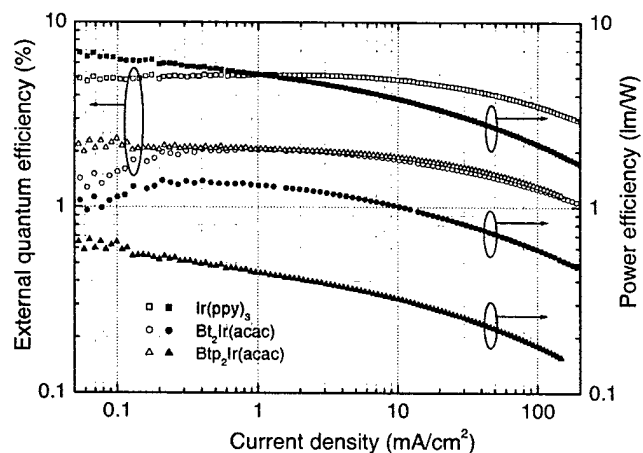
Princeton University

Blue PHOLED Performance



UNIVERSAL DISPLAY CORPORATION

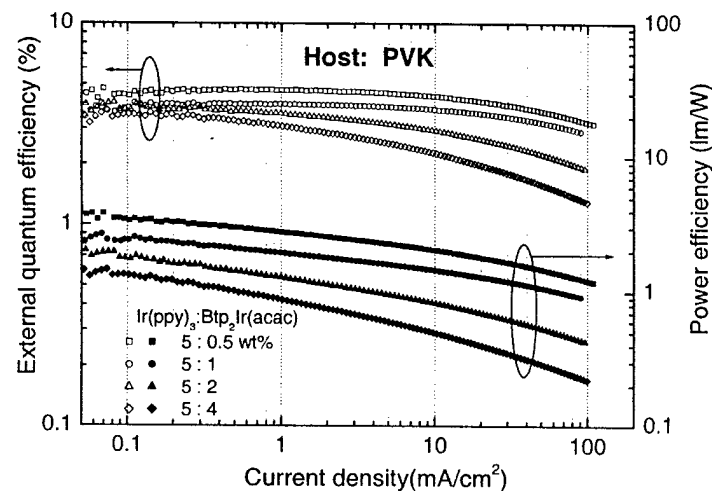
Polymer based Electrophosphorescence



Efficiencies considerably less than small molecules:
Due to low lying triplet and defect states in PVK host defeating energy transfer

Princeton University

2.5 times enhancement of red efficiency by phosphor sensitization



Princeton University

Summary of Efficiencies in EP-OLEDs

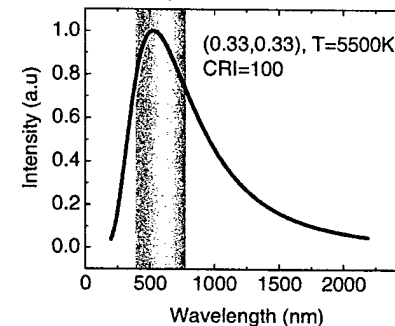
phosphor	host	Φ (lm/W)	$J = 1 \mu\text{A}/\text{cm}^2$				$J = 1 \text{mA}/\text{cm}^2$			
			η_P (lm/W)	$\eta_{Q_{\text{ext}}}$	$\eta_{Q_{\text{int}}}$	V_λ/V	η_P (lm/W)	$\eta_{Q_{\text{ext}}}$	$\eta_{Q_{\text{int}}}$	V_λ/V
ppy ₂ Ir(acac)	TAZ	530	60	0.19	0.87	0.60	20	0.15	0.68	0.25
btplr(acac)	CBP	170	4	0.07	0.32	0.34	2.2	0.06	0.27	0.22
Flrpic	CBP	260	1.3	0.006	0.027	0.83	5.0	0.057	0.23	0.34
PtOEP	CBP	60	0.3	0.056	0.23	0.09	0.2	0.042	0.19	0.08



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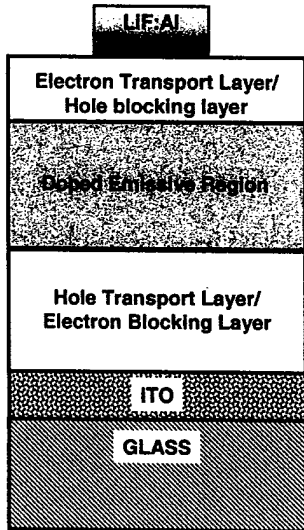
Organic White Light Emitters

- Use several dopants to achieve high efficiency via energy transfer to radiative triplet states
- Mix several dopants to attain
 - ✓ CIE chromaticity coordinates of (0.33,0.33)
 - ✓ High color rendering index Scale of 0-100



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Structure of doped OLED



Challenges for white:-

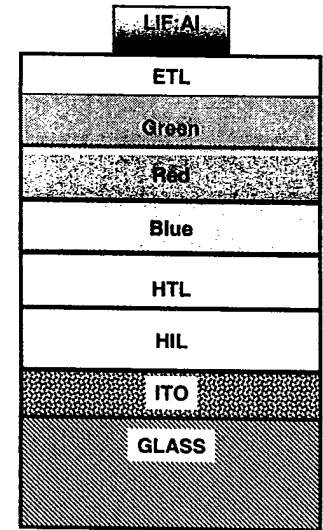
- Avoid cascade of energy from blue and green emitters to red emitter
- Tuning device color

Separating dopants into bands

- Prevent energy transfer between dopants.
- Control relative emission intensity of dopants by:
 - ✓ Varying doping concentrations (>1wt%) using thermal evaporation
 - ✓ Adjusting the thickness of bands
 - ✓ Inserting blocking layers
 - ✓ Adjusting the position of the dopants relative to the HTL

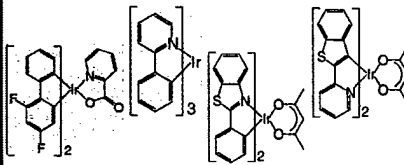
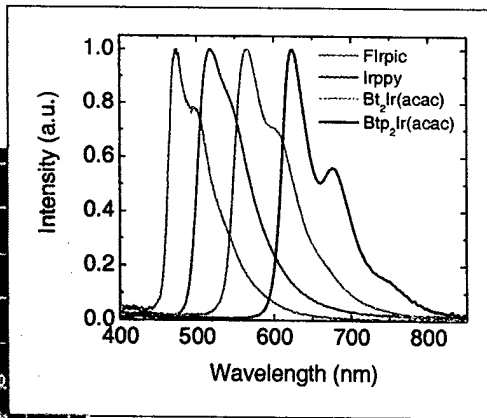
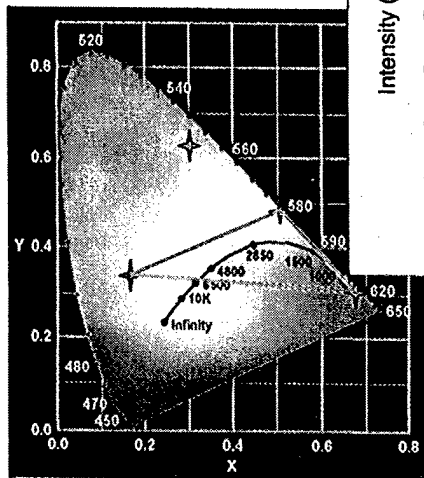
Why does it work?

- Triplets can diffuse much further than singlets (measured ~1000Å)
- Good control over diffusion of excitons using blocking layers and layer thickness

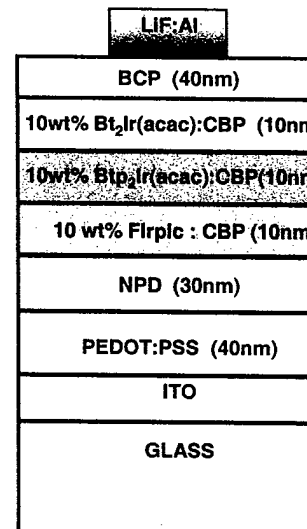


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Dopants used in WOLED

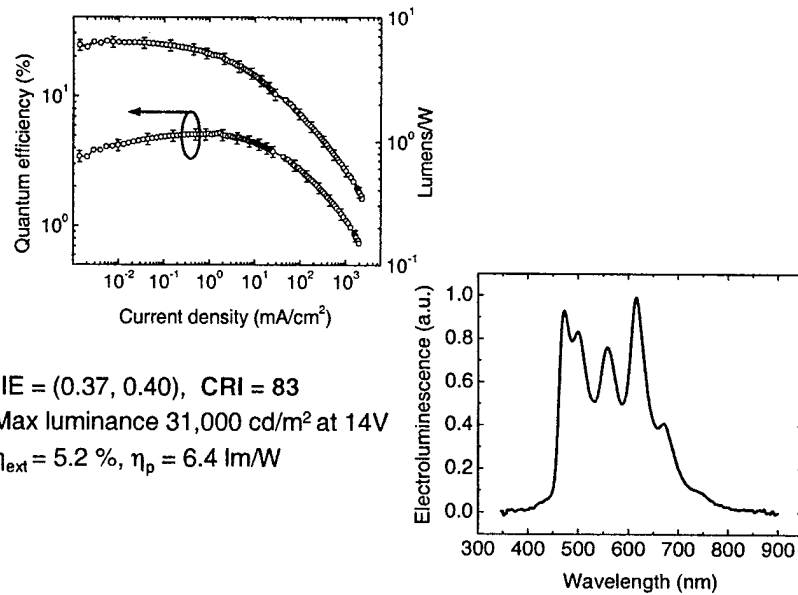
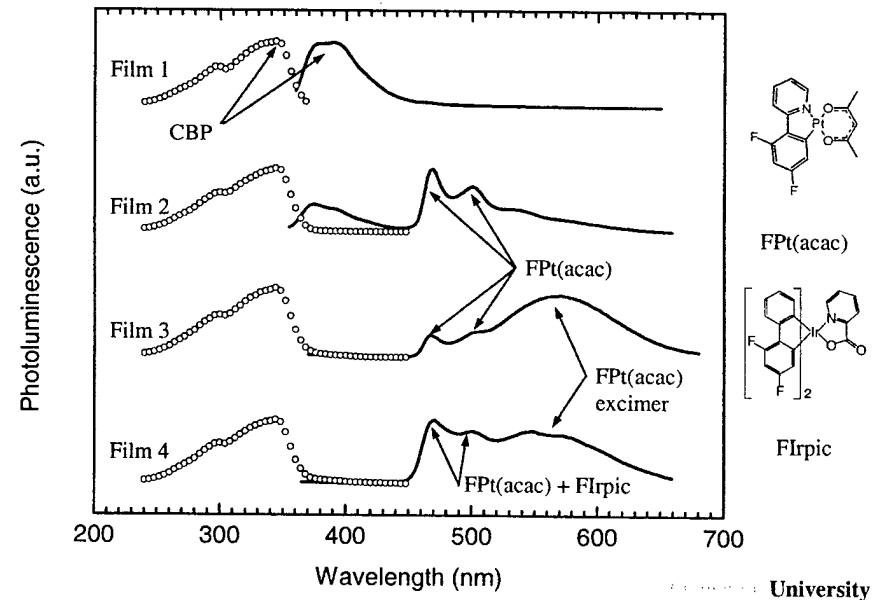


Efficient, Color Balanced White Light Emitter



3nm BCP hole/exciton blocker

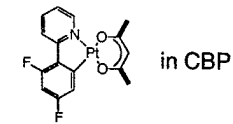
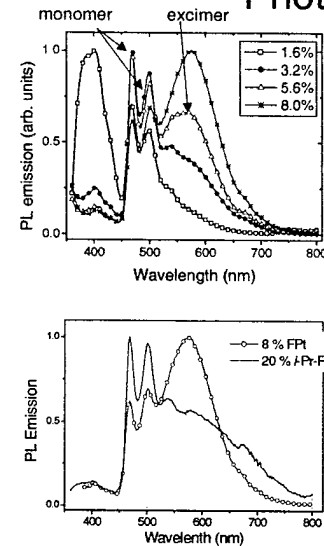
Broad Excimer Emission Simplifies Device Structure



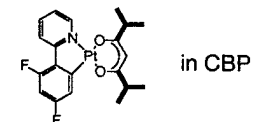
- CIE = (0.37, 0.40), CRI = 83
- Max luminance 31,000 cd/m² at 14V
 - $\eta_{\text{ext}} = 5.2\%$, $\eta_p = 6.4$ lm/W

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Single Dopant Monomer – Excimer Photoluminescence

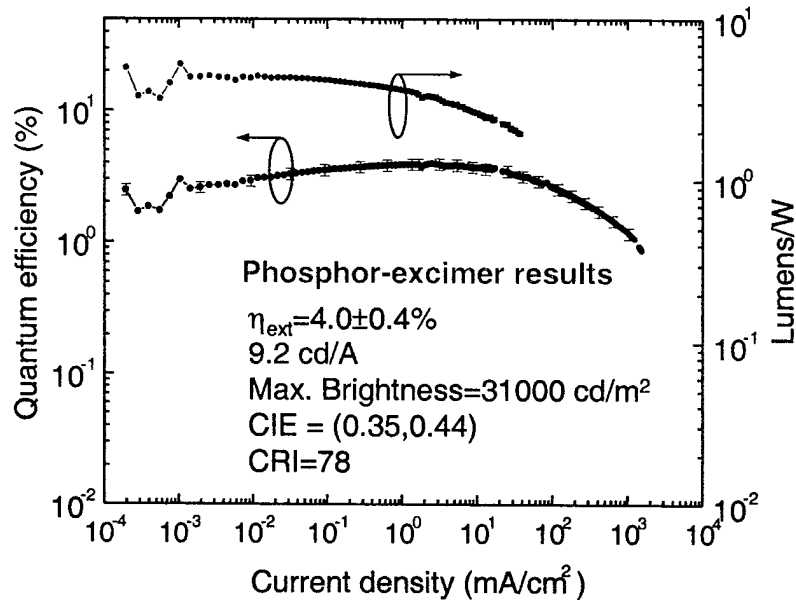


- monomer dopant emission at low doping level
- balanced monomer/excimer ~5%
- CBP fluorescence at low doping levels
- Increasing steric bulk hinders excimer formation
 - can it lead to greater monomer:excimer ratio?



- replacing methyl groups with *i*-Pr adds significant steric bulk
- Only weak excimer emission observed at doping levels as high as 20%
- too much steric bulk gives only monomer → intermediate steric bulk.

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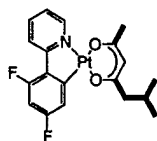


Phosphor-excimer results

$\eta_{\text{ext}} = 4.0 \pm 0.4\%$
 9.2 cd/A
 Max. Brightness = 31000 cd/m²
 CIE = (0.35, 0.44)
 CRI = 78

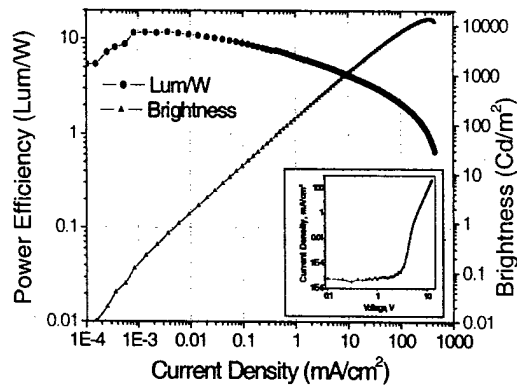
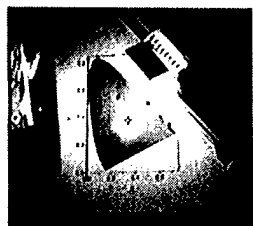
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High Efficiency Single Dopant WOLEDs



doped luminescent layer

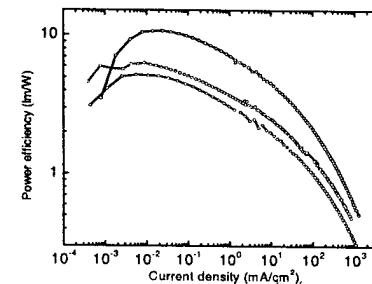
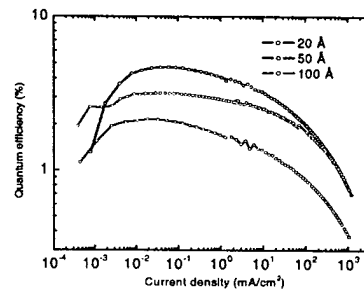
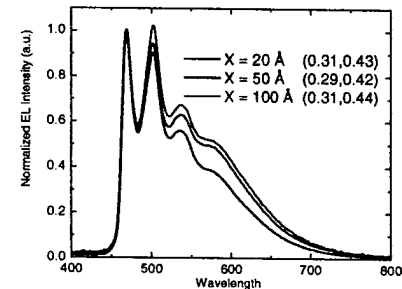
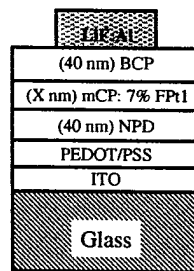
CIE: 0.39 0.41
CRI: 76



- Q.E = 5.8% , 9 lm/W @ 50 cd/m²
- Q.E = 4.5% , 5.1 lm/W @ 500 cd/m²

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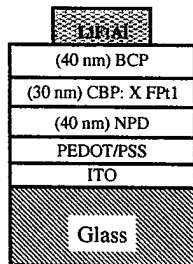
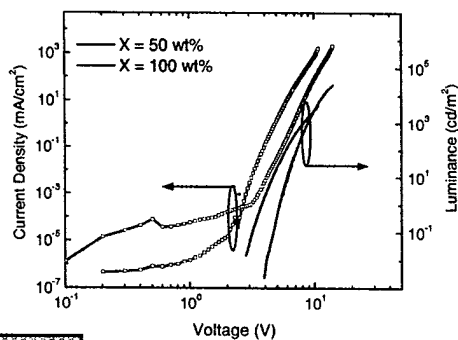
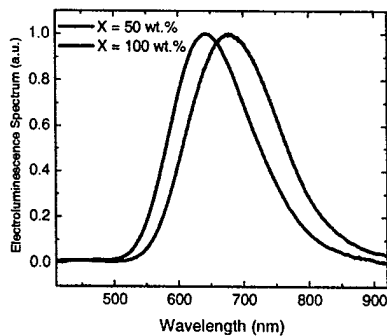
White electroluminescence spectra, J-V and luminance



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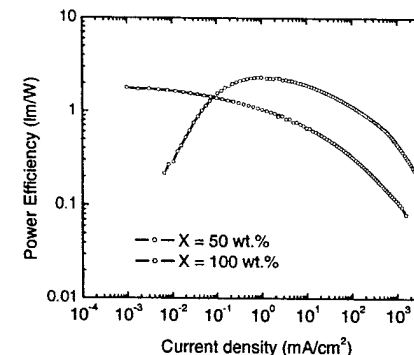
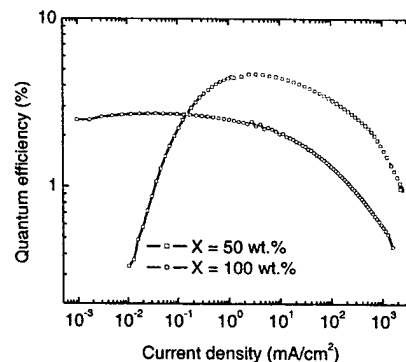
89

Red electroluminescence spectra, J-V and luminance



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Red external power and quantum efficiencies



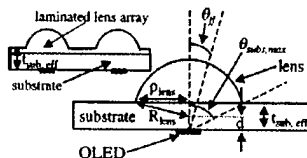
Princeton University

Low index substrates



T. Tsutsui, M. Yahiro, H. Yokogawa, K. Kawano, and M. Yokoyama, *Adv. Mater.* **13**, 1149 (2001).

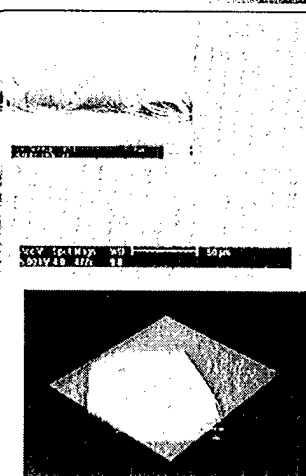
Lenses



V. Bulovic, V. B. Khalfin, G. Gu, P. E. Burrows, D. Z. Garbuzov, and S. R. Forrest, *Phys. Rev. B* **58**, 3730 (1998).

Picture: C. F. Madigan, M. H. Lu, and J. C. Sturm, *Appl. Phys. Lett.* **76**, 1650 (2000).

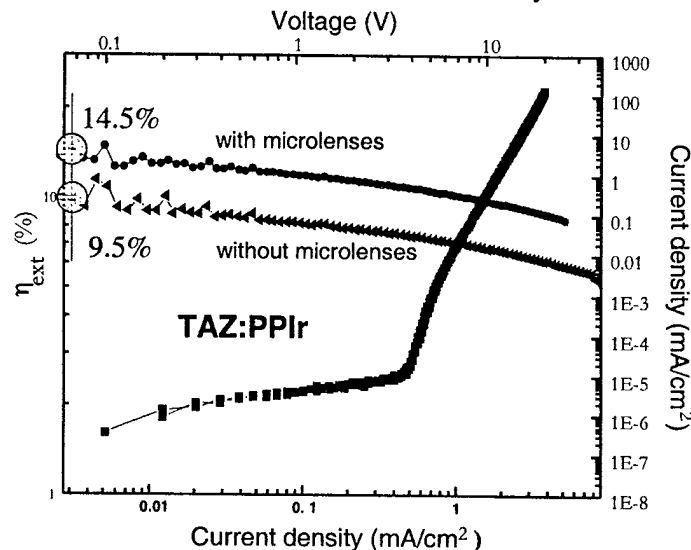
Optical elements



S. Möller and S. R. Forrest, *MRS Fall Mtg.*, (2001), Paper BB.6.9

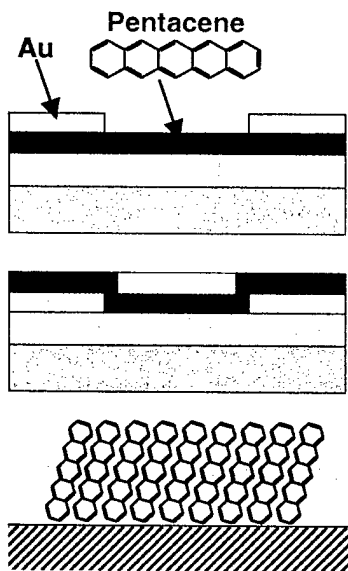
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External Quantum Efficiency



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Thin Film Transistors with Pentacene Channels



“Top-contact”

Long ($>10\mu\text{m}$) channels
Shadow Masking /
Cold-Welding

“Bottom-contact”

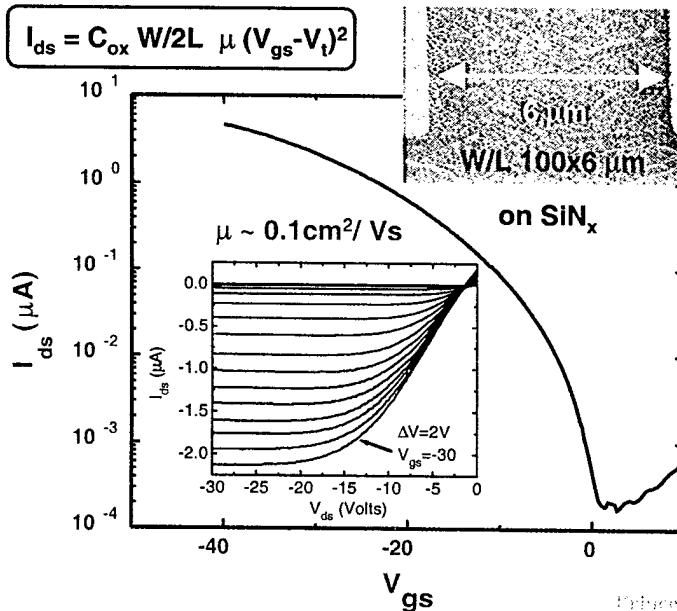
Shorter channels
Photolithography

Charge Transport

Along π overlap
Trap-limited

University

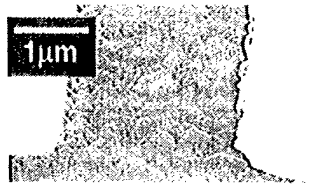
Pentacene TFTs by OVPD, Bottom Contact



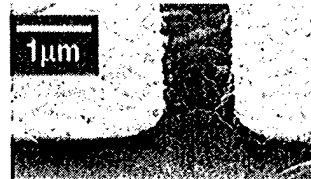
University

Reaching Single-Crystal mobility with BC geometry

a. reduce channel length → “fails”
 b. increase grain size

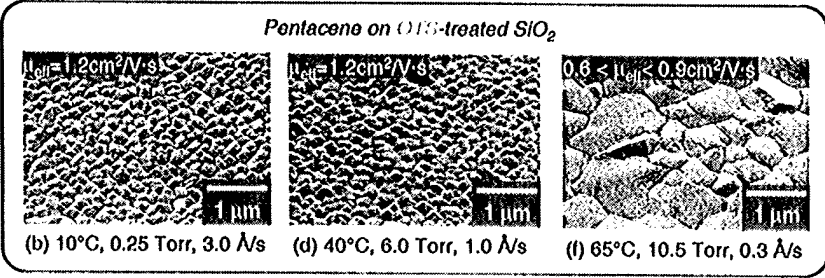
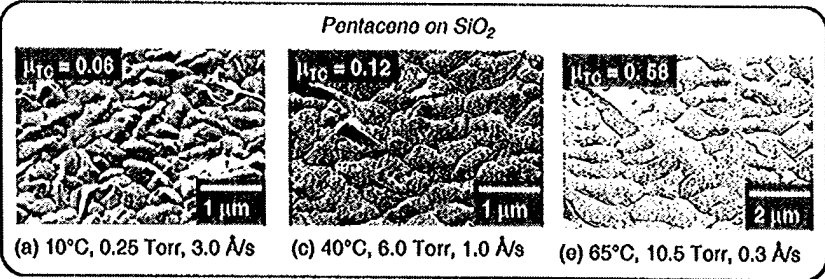


0.8 Torr
 10°C
 grain < 1 μm
 L = 2 μm
 → μ = 0.1
Bottom contact

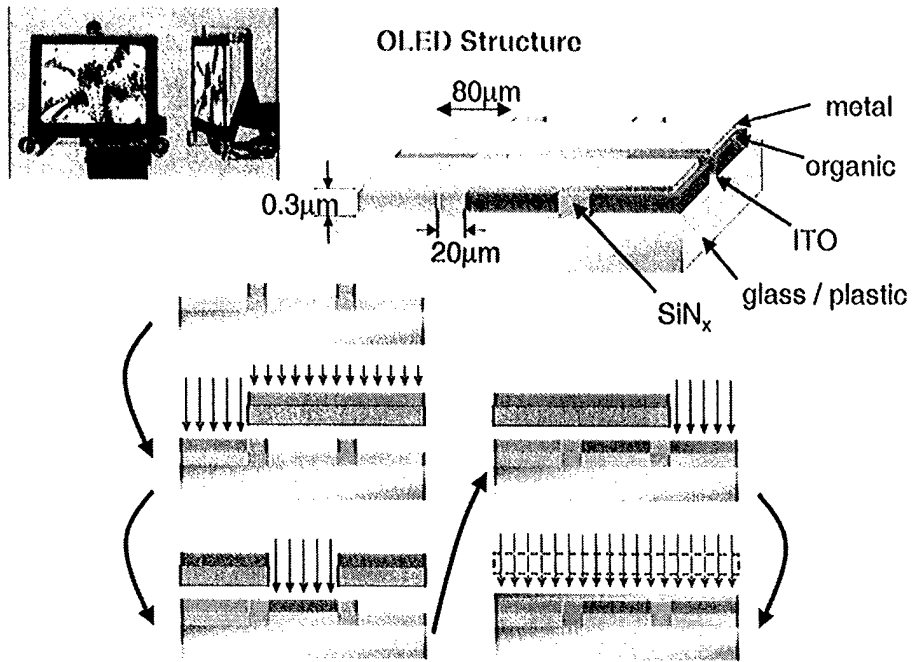


8 Torr
 65°C
 grain > 1 μm
 L < 1 μm
 → μ = 0.01
Bottom contact
 OTS-treated SiO₂
 μ < 2 cm²/Vs
 * Jackson et al.

Controlling Pentacene Film Morphology - Top Contact Geometry

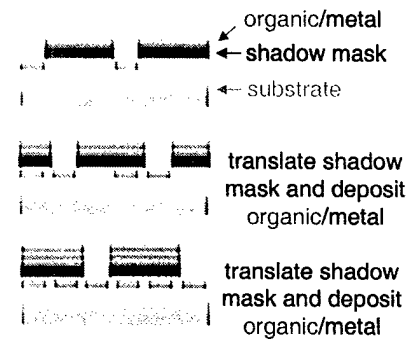


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Patterning of Full Color Displays

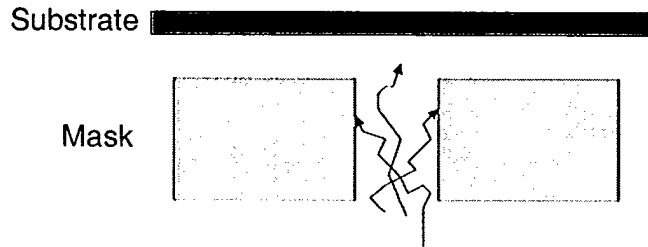
• Conventional shadow mask technique



Limitations:

- Resolution determined by mask thickness
- Requires integrated shadow mask (ISM)
- Requires precise positioning

Growth through apertures



- Will surface absorption prevent deposition at the substrate?
- What pattern resolution is achievable?

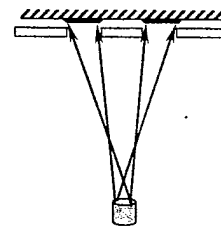
Patterned deposition through masks necessary for full color displays and other applications

University

Micropatterning of organic thin films: experiment

Mask thickness = $7\mu\text{m}$
Aperture = $7.5\mu\text{m}$

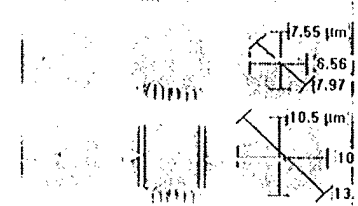
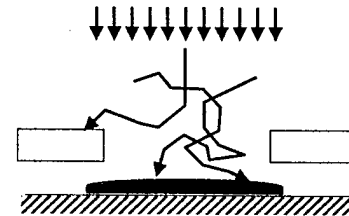
Mask separation $3\mu\text{m}$
Carrier velocity 1 m/s



Evaporation at 10^{-6}Torr

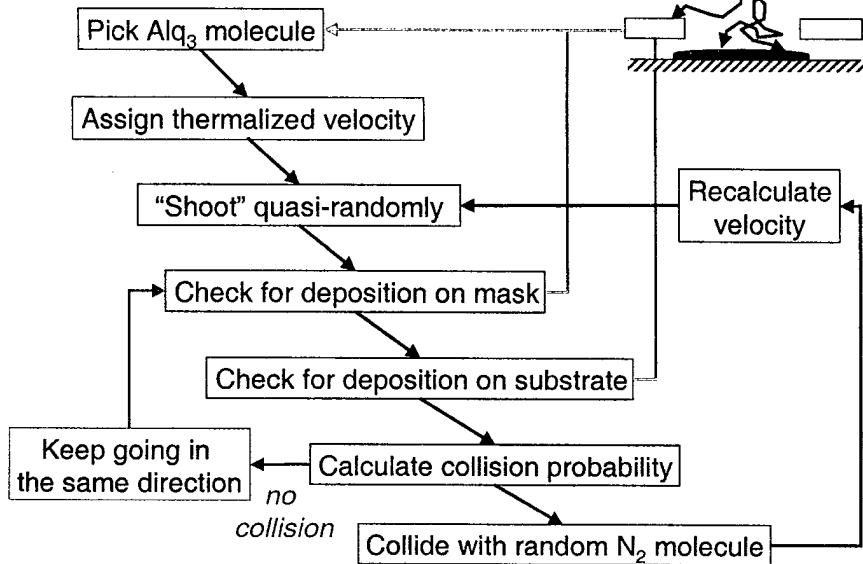


OVPD at 0.1 Torr



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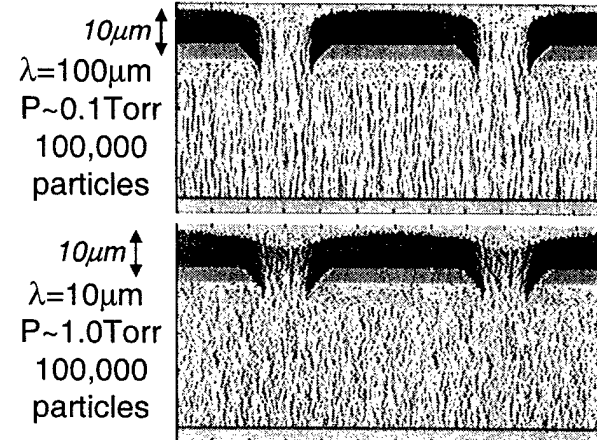
Monte-Carlo Simulation Algorithm



University

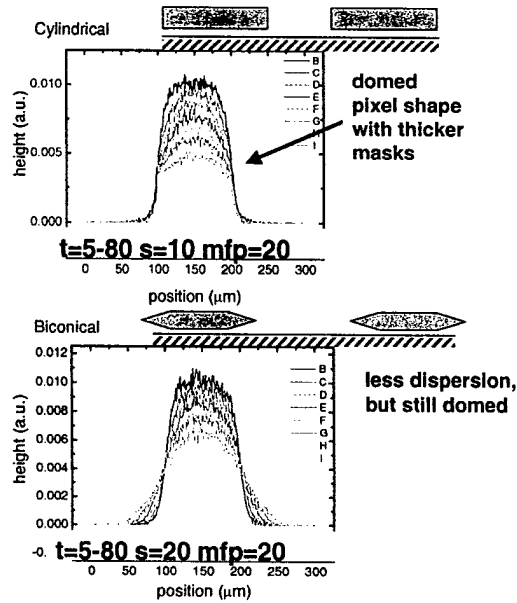
Alq₃ film deposition in N₂ background

pattern evolution in time



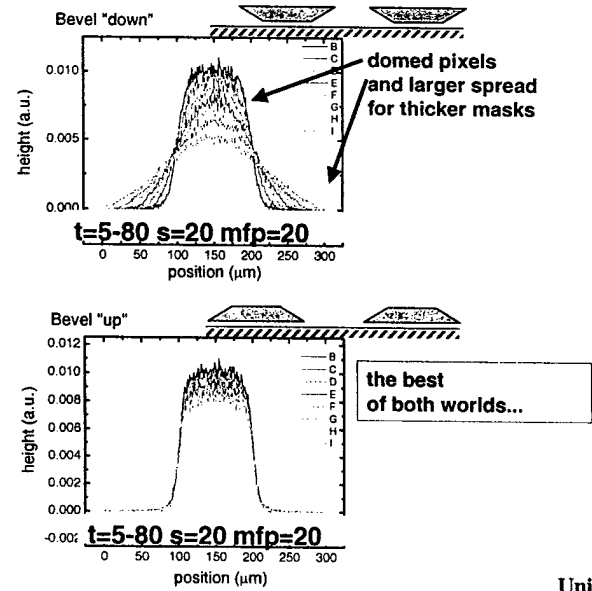
University

Effect of masking geometry on pixel shape



University

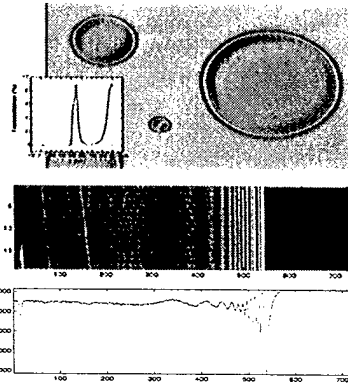
Effect of masking geometry on pixel shape



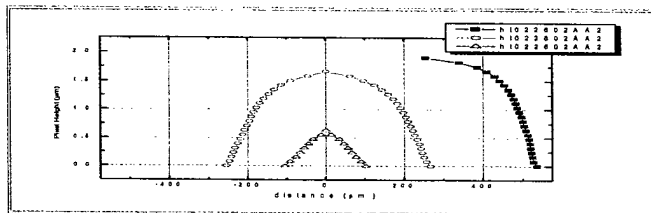
University

Experimental determination of pixel shape

1. Microscope w/ monochromatic light source

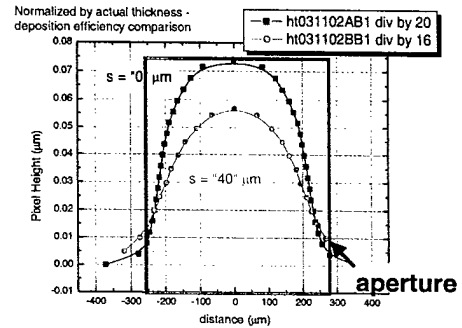
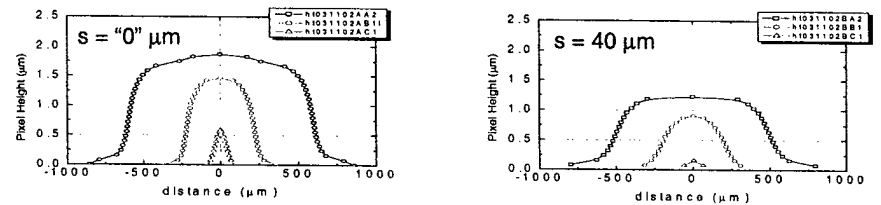


2. Digitize image and count fringes



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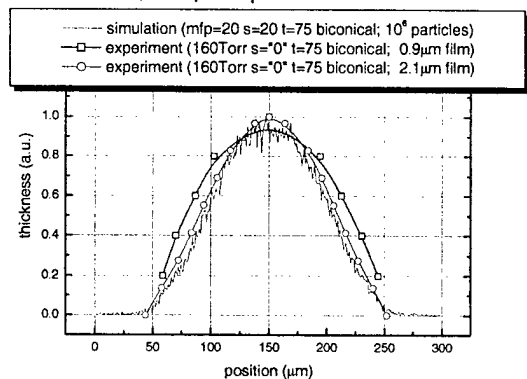
Example: cylindrical aperture, 0.16 Torr vary pixel size, vary separation



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Smaller patterns & comparison w/ simulation

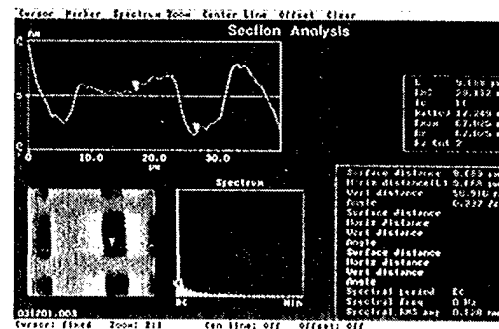
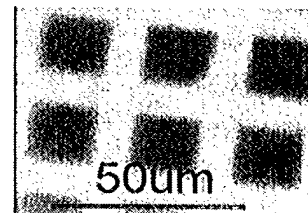
Biconical Mask, 100 μ m aperture



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Really small patterns \rightarrow AFM

@ 1.4Torr



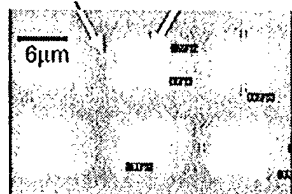
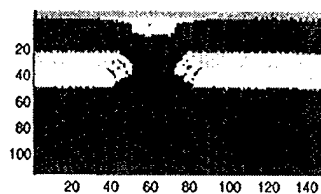
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Hybrid OVPD + vacuum Deposition

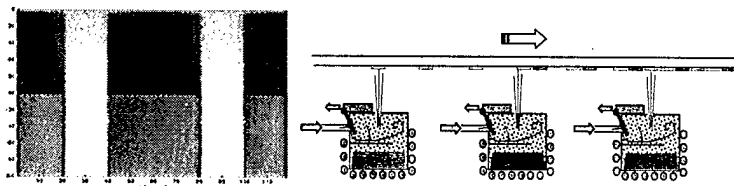
$\lambda=5\mu$ m

OVPD @ 1 Torr

VTE @ 10⁻⁶Torr

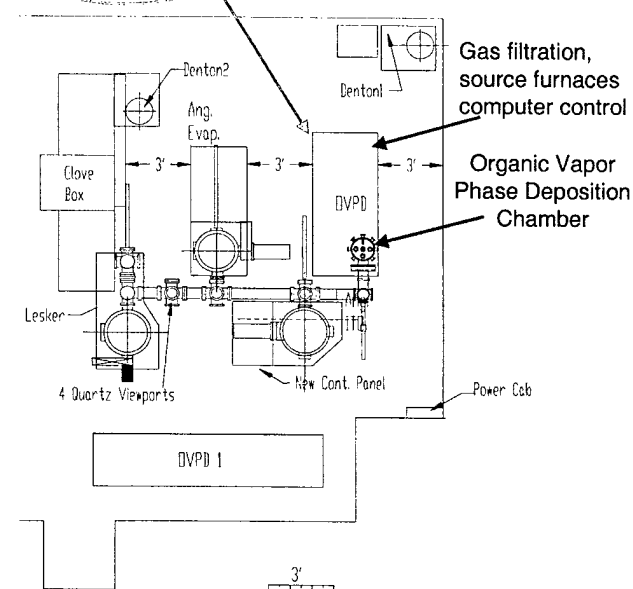


Organic vapor jet deposition: for home office?



University

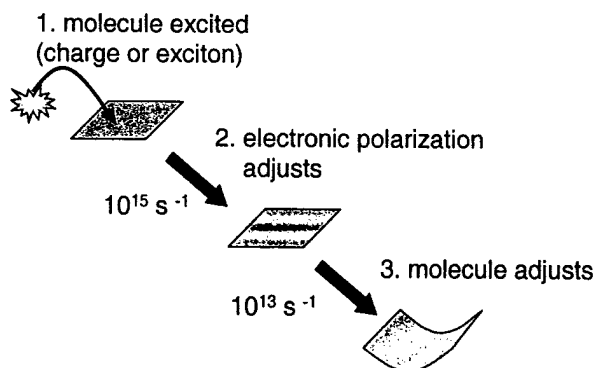
Full lab layout with new OVPD system



University

INTRODUCTION TO ELECTRON TRANSFER

Incoherent energy transfer



Born-Oppenheimer approximation:

electronic motion is much faster than nuclear motion.

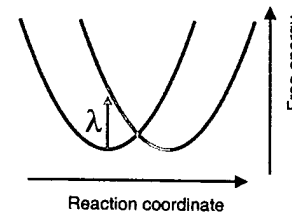
Rate of energy and charge transfer is limited by nuclear motion, and the reconfiguration of the molecules

sity

Marcus electron transfer

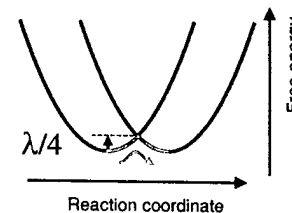
Represent molecules as simple harmonic oscillators.
 Intermolecular overlap energy is small $\sim 10 \text{ meV}$.

Both molecules in relaxed state:



Reorganizational energy required = λ

If both molecules adjust:



Reorganizational energy required = $\lambda/4$

Typically, $\lambda \sim 0.1 - 0.5 \text{ eV}$.

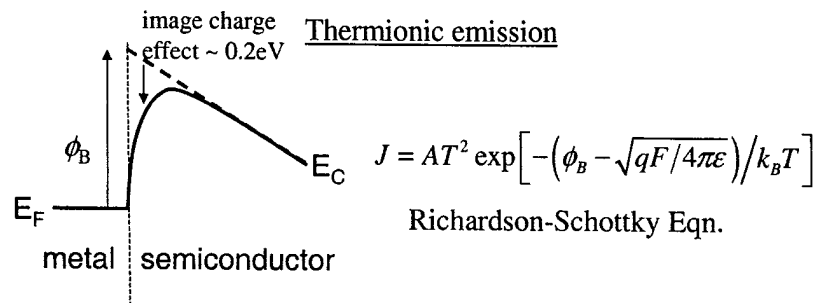
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INJECTION LIMITED MODELS

Thickness dependence of transport in Alq_3 is injection limited for thin films ($d < 2000 \text{ \AA}$).

Traditionally semiconductor injection is analyzed following thermionic injection or tunneling injection.

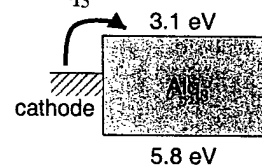
Injection is strongly temperature dependent: eliminating tunneling injection.



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PROBLEMS WITH THERMIONIC EMISSION

Examine different cathodes on Alq_3 .



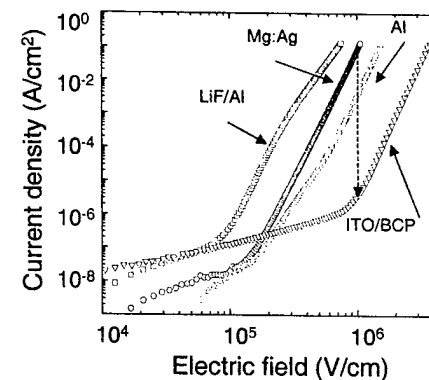
Work functions:

Mg: 3.7 eV

Al: 4.0 eV

Indium tin oxide (ITO): 4.7 eV

From work function alone, we expect 1eV difference between Mg and ITO to reduce injection by factor of 10^{18} , actually only 10^5 .

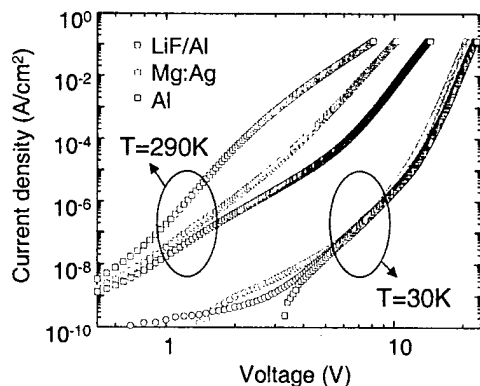


L.S. Hung et al. Appl. Phys. Lett. **70**, 152, 1997

G. Parthasarathy et al. Appl. Phys. Lett. **76**, 2128, 2000

University

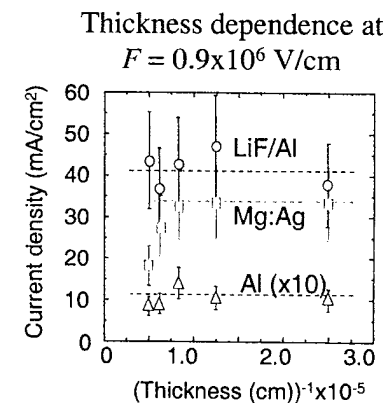
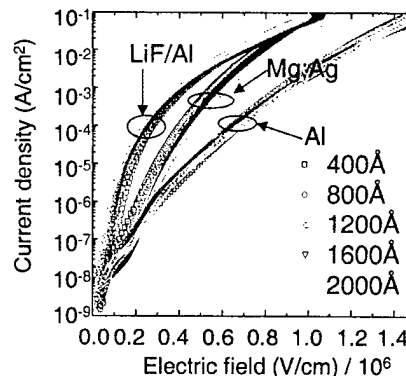
NO CATHODE DEPENDENCE AT LOW TEMPERATURES



Transport is injection limited for $T < 300\text{K}$.

But transport is independent of cathode at low temperature - injection must depend on interfacial organic layers.

THICKNESS DEPENDENCE (II)

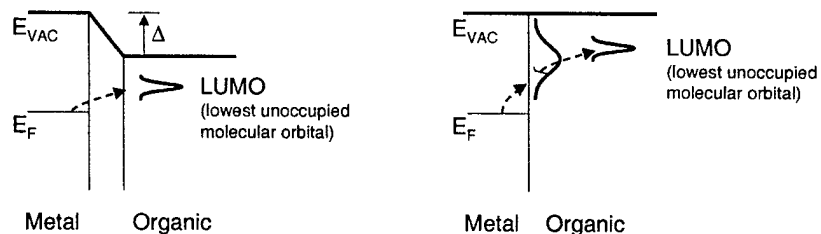


If transport is space charge limited (bulk limited), $J \sim 1/d$, irrespective of field dependence of mobility.

Characteristics are consistent with injection-limited transport.

THE METAL/ORGANIC INTERFACE

Reasons why the metal work function may not be an accurate measure of cathode injection efficiency.

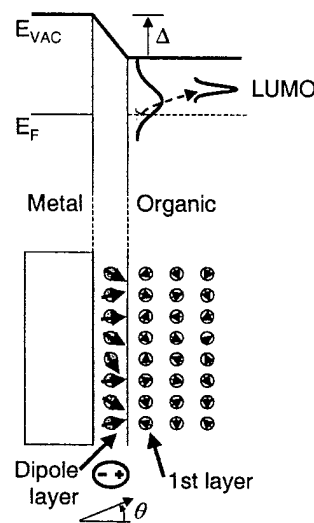


An interfacial dipole may shift the surface energy of the organic film

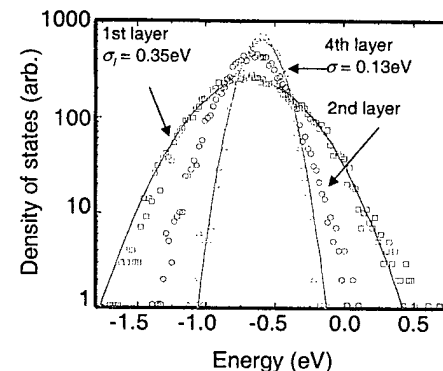
Intermediate states may reduce the overall hopping barrier

The presence of an interfacial dipole induces the intermediate states

DISORDER IN THE INTERFACIAL DIPOLE



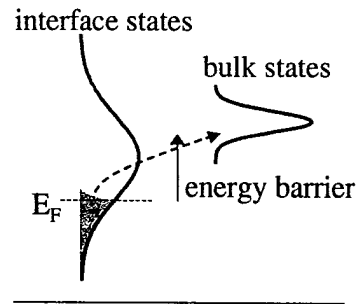
Assuming interfacial dipoles of strength $\sim 30\text{D}$, and Gaussian orientation disorder with variance $\sigma = \pi$ radians, we get:



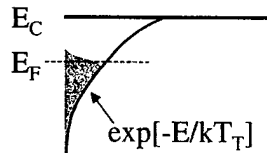
Alternately, disorder may be due to local variation in magnitude of dipoles

FEATURES OF THE INTERFACIAL STATE MODEL

- Limiting step is hop from organic interface to organic bulk
- Transport can be explained using only intrinsic properties
No need for extrinsic effects such as traps.
- Broad distribution of interface states generates power law transport
- similar to trapped charge limited transport (distribution of states below a conduction level)



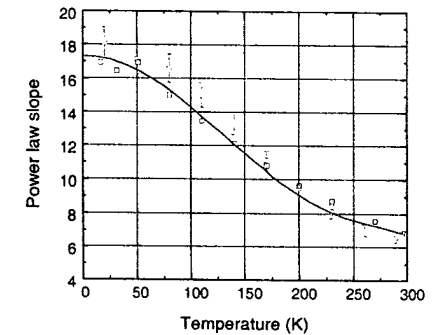
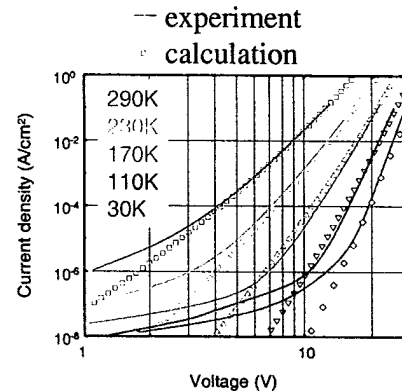
Classical trap charge limited conduction



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TEMPERATURE DEPENDENCE OF Mg:Ag/Alq₃ INTERFACE

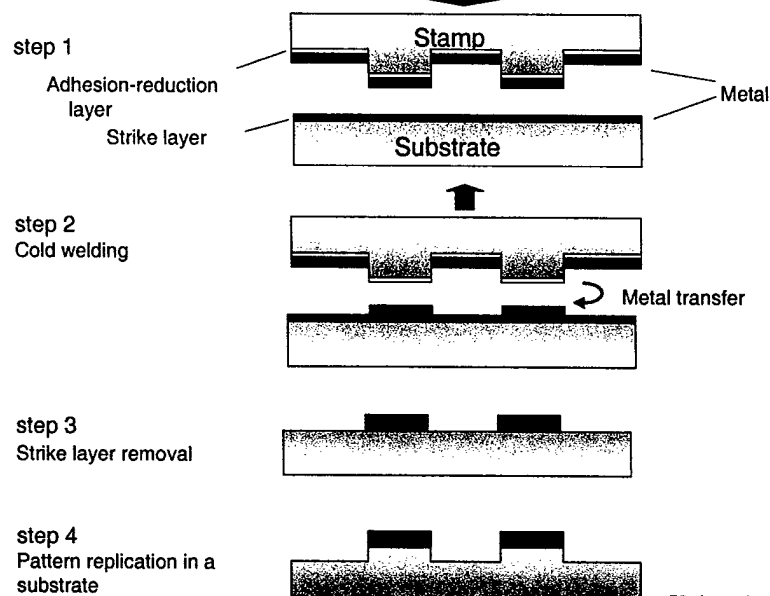
Device: 300Å Ag / 1000Å 25:1 Mg:Ag / 1200Å Alq₃ / 1000Å Mg:Ag / SiN_x / Si



Fit using polaron model for interfacial hop:
includes temperature dependence of phonon distribution

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Additive Cold-welding Process



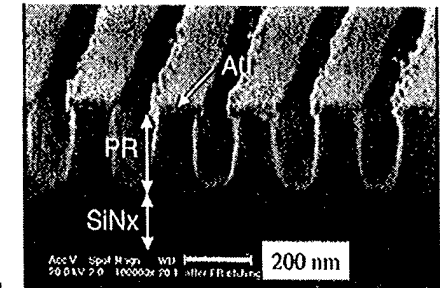
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Cold-welding for high resolution lithography

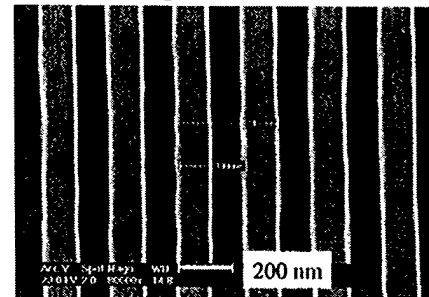
stamp

substrate: Si/SiN_x/PR/
stamp: Si/Alq₃/
"parting layer"

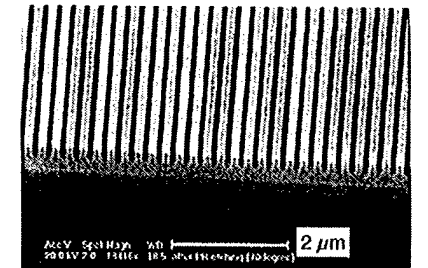
200 MPa, 10 MPa/s, no hold time.
Au etch : Ar sputtering
PR etch : O₂ RIE



photoresist layer is etched

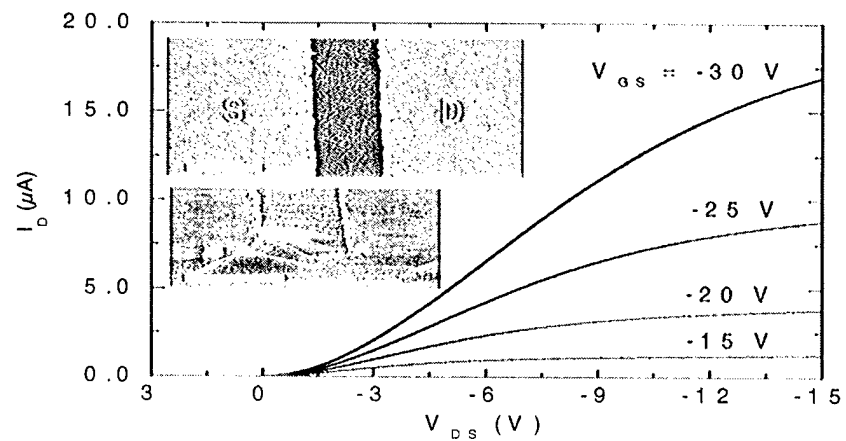


transferred metal lines



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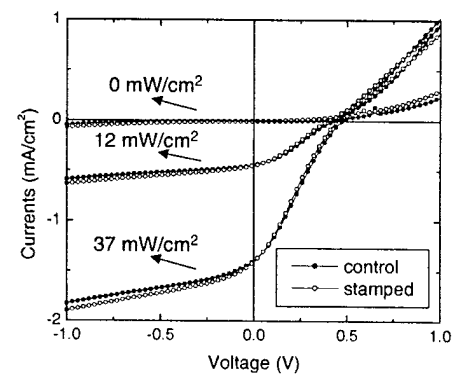
Additive Cold-welding for Narrow Gate OTFTs



$L=1\ \mu\text{m}$
 $\mu\sim 0.1\ \text{cm}^2/\text{V}\cdot\text{s}$

University

Additive Cold-welding for Organic Solar Cells



University

Advances in Chemistry of Materials for OLEDs

Mark Thompson
USC

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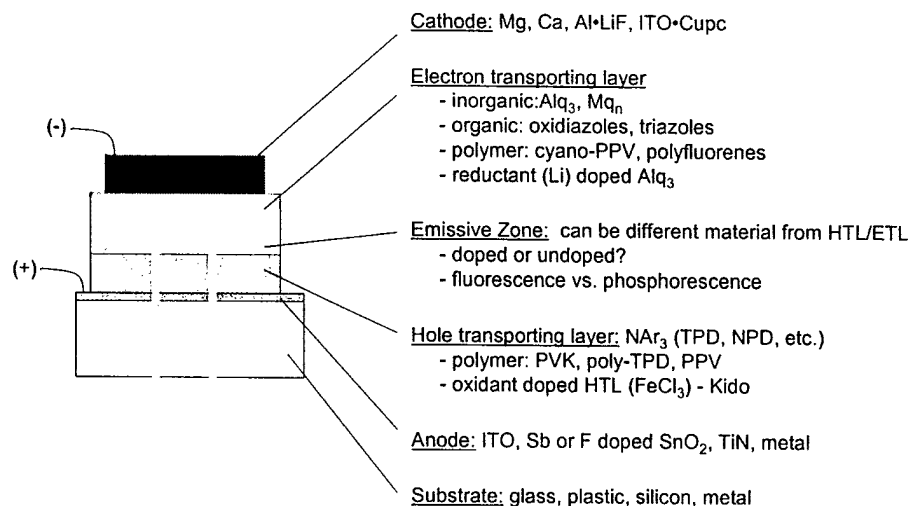
Library of diamines

$T_g, T_m, E_{ox}, PL(\lambda_{max}), abs(\lambda_{max})$

Chemical Structure	C	N _a	N _b	D	T	B	S
CCP	215.88	212.83	158.61	159.54	233.91	259.103	259.103
310NA	1.041	0.945	0.965	0.950	0.958	1.008	1.008
255.310	255.310	285.295.320	295.320	295.320	295.315	295	270.310
343	415	409	409	370	382	393.887	
N _a N _b P	N _a N _b P	N _a N _b P	N _a N _b P	N _a N _b P	N _a N _b P	N _a N _b P	N _a N _b P
185.90	185.90	185.90	185.90	185.90	185.90	185.90	185.90
0.675	0.616	0.611	0.595	0.551	0.591	0.591	0.591
280.320	280.320	320	320	315	300.350	300.350	300.350
365	399.496	414.201	412.206	395.210	407		
DN _a P	DN _a P	DN _a P	DN _a P	DN _a P	DN _a P	DN _a P	DN _a P
182.68	182.68	182.68	182.68	182.68	182.68	182.68	182.68
0.616	0.606	0.592	0.569	0.581	0.581	0.581	0.581
250.330.325	320	320	280.330	280.315	280.315	280.315	280.315
471	399.495	398.470	398.475	402			
DDP	DDP	DDP	DDP	DDP	DDP	DDP	DDP
290.15A	109.22	250.56	304.66	304.66	304.66	304.66	304.66
0.602	0.593	0.560	0.563	0.563	0.563	0.563	0.563
320.340	315	310.350	310	310	310	310	310
394	397	437	398	398	398	398	398
TTP	TTP	TTP	TTP	TTP	TTP	TTP	TTP
175.99	175.99	175.99	175.99	175.99	175.99	175.99	175.99
0.561	0.574	0.558	0.558	0.558	0.558	0.558	0.558
315	320	315	315	315	315	315	315
376	398	400	400	400	400	400	400
BBP	BBP	BBP	BBP	BBP	BBP	BBP	BBP
NA/73	NA/73	NA/73	NA/73	NA/73	NA/73	NA/73	NA/73
0.492	0.416	0.416	0.416	0.416	0.416	0.416	0.416
310	310	310	310	310	310	310	310
368	368	368	368	368	368	368	368
SSP	SSP	SSP	SSP	SSP	SSP	SSP	SSP
304	304	304	304	304	304	304	304
0.489	0.489	0.489	0.489	0.489	0.489	0.489	0.489
290.340	290.340	290.340	290.340	290.340	290.340	290.340	290.340
444.488	444.488	444.488	444.488	444.488	444.488	444.488	444.488

D. E. Loy, et. al., *Chemistry of Materials*, 1998, 10, 2235-2250.

Heterostructure OLEDs



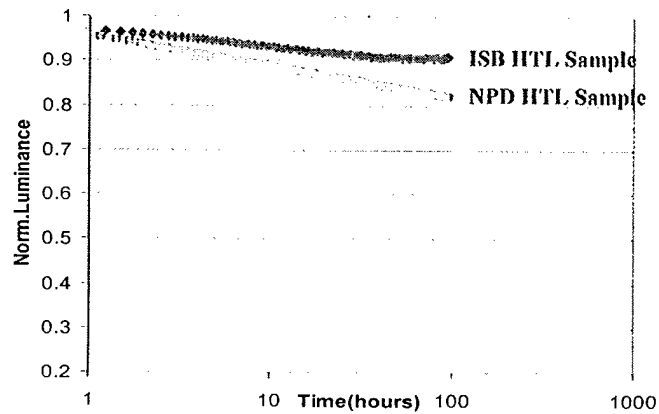
Diamine Hole Transporters in OLEDs

Compound	Chemical Structure	T _g (°C)	Potential relative to TPD, TPD = 0.715 V	η (%)	Voltage @ 0.1 mA
ISB		115	-0.044	0.65	9.6
IDB		110	-0.008	0.12	16
TPD (standard)		65	0	0.44	9.8
BCB		110	0.029	0.65	12.3
NTB		85	0.076	0.65	8.7
NPD (standard)		95	0.197	0.75	9.4
NCB		109	0.273	0.25	11.1
Alq ₃		175	0.30		

- Device structure: ITO/HTL (400 Å)/Alq₃ (400 Å)/Mg-Ag
- ISB has the best combination of efficiency and low voltage operation (similar to NPD), highest T_g
- D F. O'Brien, et. al., *Advanced Materials*, 1998, 10, 1108-1112.

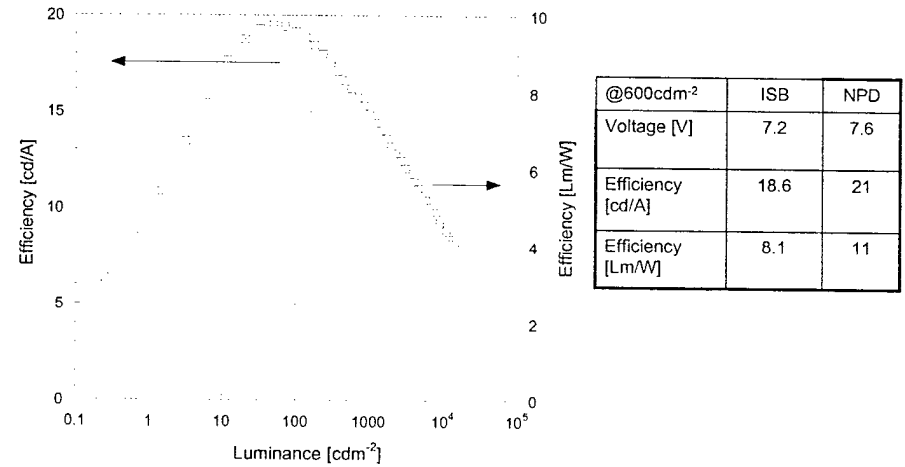
High T_g HTL Lifetime Comparison

ITO/CuPc(100A)/HTL(500A)/CBP:PtOEP(300A)/Alq₃(200A)/MgAg



UNIVERSAL DISPLAY CORPORATION

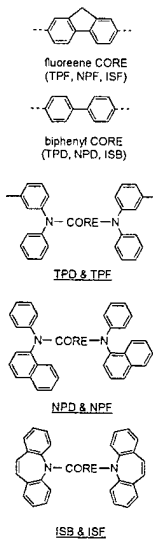
G1 structure with ISB as a HTL Efficiency vs. luminance



UNIVERSAL DISPLAY CORPORATION

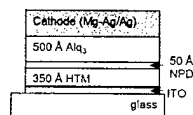
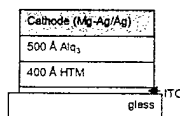
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Fluorene Cored HTLs



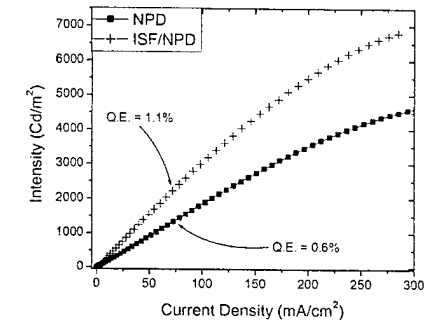
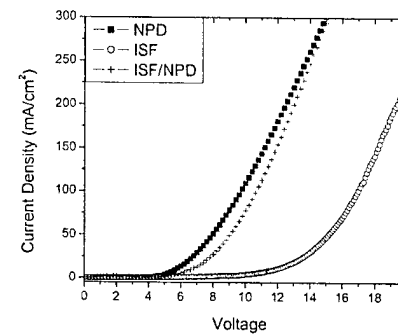
Material Acronym	TPF	TPD	NPF	NPD	ISF	ISB
T _g (°C)	78	60	118	95	161	115
1 st Oxidation (vs. Ag/AgCl)*	0.626	0.733	0.658	0.767	0.516	0.699
Absorption/Emission (nm)	340/398	315, 355/396	360/470	270, 340/450	295/530	300/530

- Fluorene core gives higher T_g than biphenyl
- Lowers oxidation potential: raises HOMO energy
- What about OLEDs?



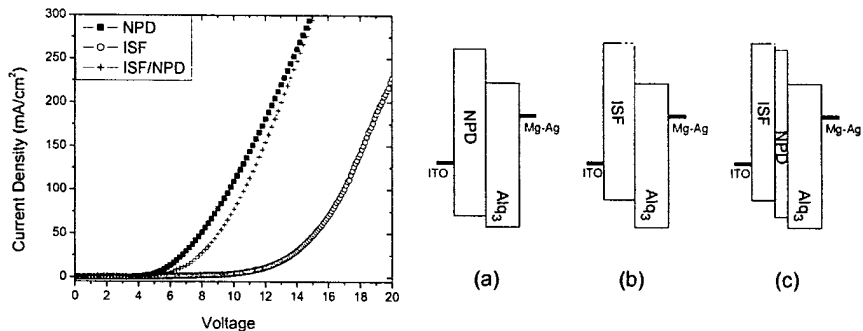
D. Loy, et. al., *Adv. Func. Mat.*, 2002, 12, 245.

ISF based OLEDs



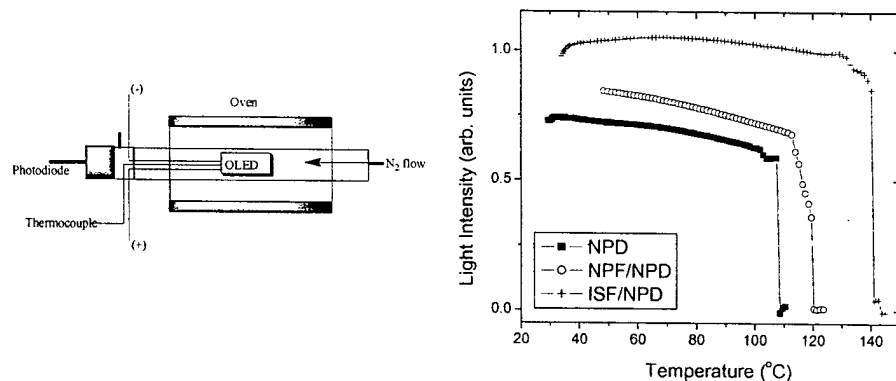
- NO LIGHT for ISF/Alq₃ device
- NPD interface layer is needed to efficiently inject holes from ISF to Alq₃
- ISF HOMO is too shallow

ISF based OLEDs



- NO LIGHT for ISF/Alq₃ device
- NPD interface layer is needed to efficiently inject holes from ISF to Alq₃
- ISF HOMO is too shallow

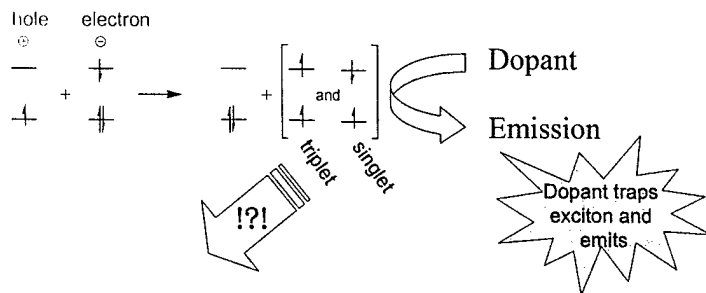
Thermal Stabilities



- ISF/NPD HTL crashes 45°C above the NPD T_g
- Low T_g interface layer is not a problem!

8

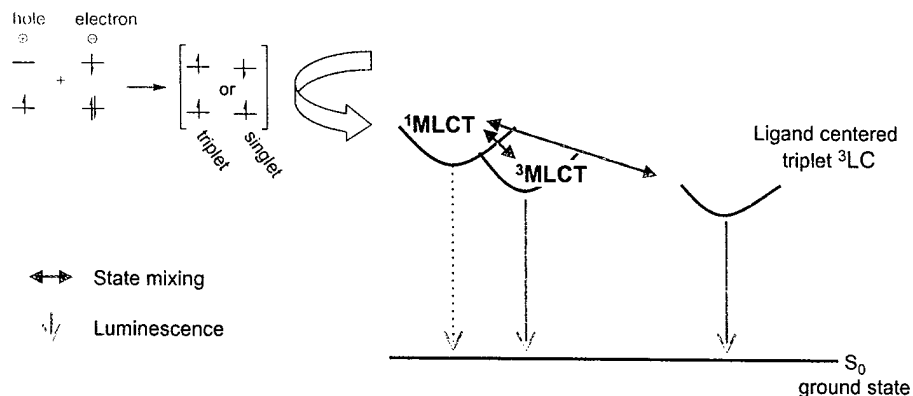
Hole/electron recombination leads to singlet and triplet excitons



- Expected singlet fraction based on simple spin statistics = 25%
- Energy transfers from host/matrix excitonic states to dopant conserve spin.
- Phosphorescence (triplet emission) is formally a forbidden process.

Experimentally determined singlet fraction for Alq₃ based OLEDs = 22±3%
M.A. Baldo, et al., Phys. Rev. B (1999)

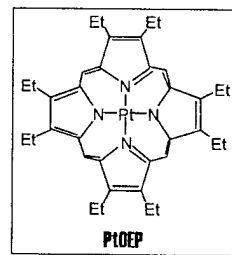
Heavy metal facilitated triplet emission



- Strong spin-orbit-coupling mixes singlet and triplet MLCT states, for M = Ir, Pt, Os, Re, etc.
- Mixing of triplet states with 1MLCT makes phosphorescence a largely allowed transition, short triplet lifetime

Pt based phosphorescent dye/dopant

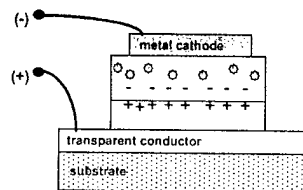
- Platinum octaethylporphine (PtOEP) has high phosphorescence quantum efficiency*
 - PL efficiency (phosphorescence) is 0.5 at 298 K (in polystyrene), $\tau = 91$ msec
 - PL efficiency 0.9 at 77K, $\tau = 130$ msec



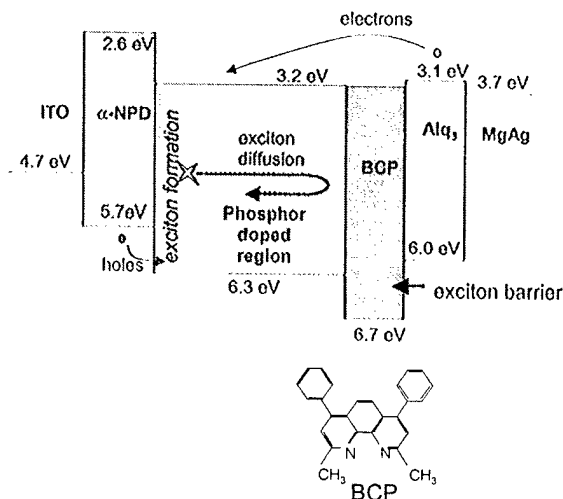
- Simple, two layer structure gives good eff.
 - 4 % external at low brightness
 - Exclusive PtOEP triplet emission.

See: M.A. Baldo, et al., *Nature* (1998)

- G. Ponterini, et al, *J. Am. Chem. Soc.*, (1983)
- D.B. Papkovski, *Sens. Actuators*, (1995)
- J. Rodriguez, et al, *Chem. Phys. Lett.*, (1988)



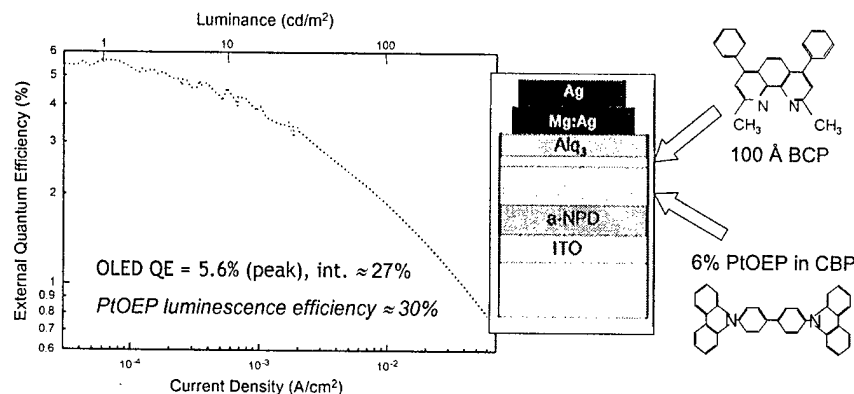
Efficient electrophosphorescent device structure



- Triplet excitons have long lifetimes, leading to long exciton diffusion lengths
 - > 1400 Å for PtOEP
- Blocking layers:
 - prevent exciton diffusion to the electrodes and quenching
 - Confine carrier recombination to the emissive layer

8

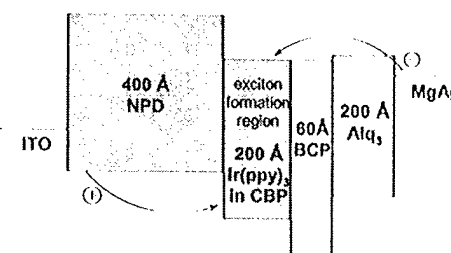
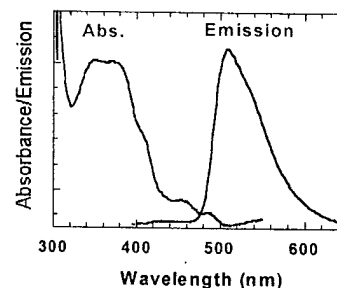
Quantum Efficiencies of PtOEP OLEDs with an Exciton Blocking Layer



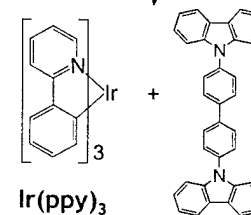
- Q.E. decay as current is increased is due to T-T annihilation
 - $T_1 + T_1 \rightarrow S_0 + S_1$, second order quenching process !!
 - decrease the effects of T-T annihilation by:
 - decrease [triplets], lower the doping level: phosphor saturation a problem
 - short triplet lifetime will decrease T-T annihilation

See: D. O'Brien, et al., *Appl. Phys. Lett.* (1999)

Organometallic Ir Phosphor

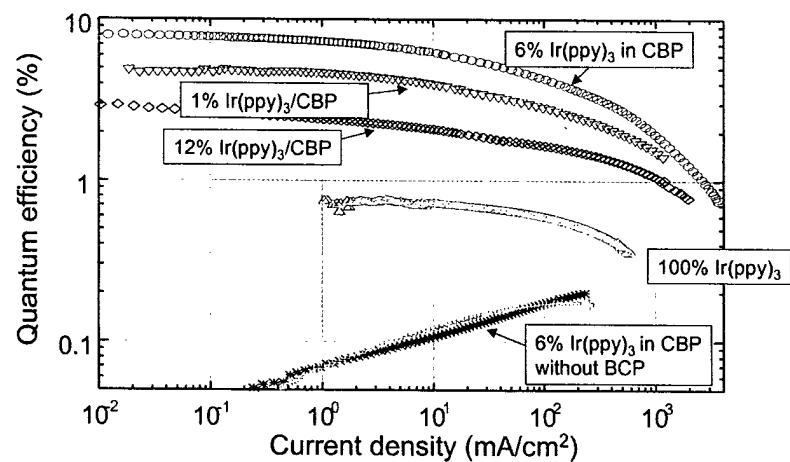


- short lifetime: 500ns in CBP
- no fluorescence observed, only phosphorescence ($\phi_{PL} = 0.4$) Iridium \Rightarrow strong intersystem crossing
- R.J. Watts, et al., *Inorg. Chem.* (1991)



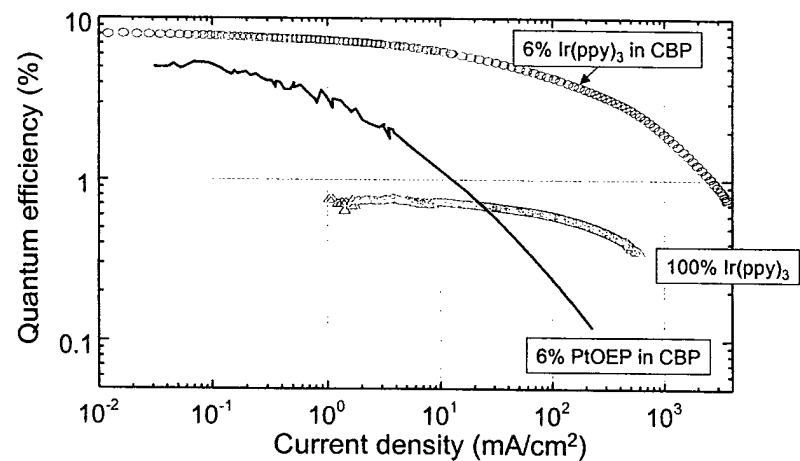
M.A. Baldo, et al., *Appl. Phys. Lett.*, 1999

External quantum efficiency of Ir(ppy)₃ in CBP



- ca. 1/5 of the light is forward scattered, thus $\eta(\text{internal}) = 5 \times \eta(\text{external})$
peak internal efficiency $\approx 40\%$

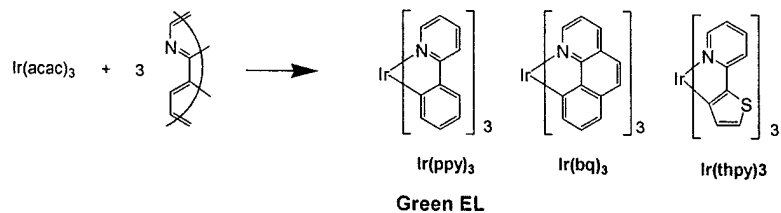
External quantum efficiency of Ir(ppy)₃ vs. PtOEP in CBP



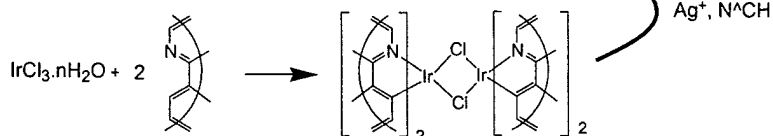
- PtOEP and Ir(ppy)₃ devices have the same structure.

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Synthesis of Cyclometallated Ir Complexes

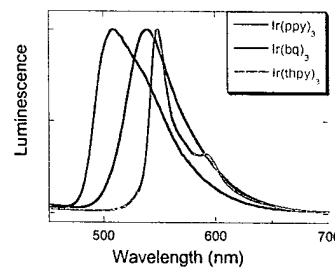


typical yield = 30%, reaction only works for ppy, bq and thpy
 Ir(ppy)₃: R.J. Watts, et. al., *Inorg. Chem.*, (1991)



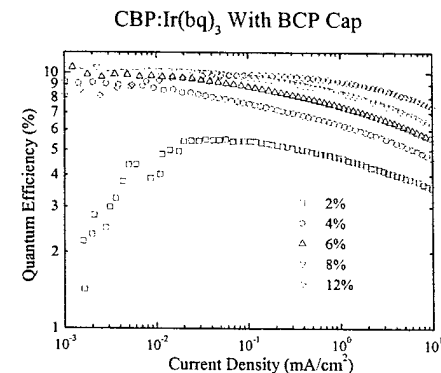
typical yield > 90%, not emissive in solution or solid state
 M. Nonoyama, *Bull. Chem. Soc. Jpn.* (1974)

Electroluminescent Spectra of Cyclometallated Phosphors



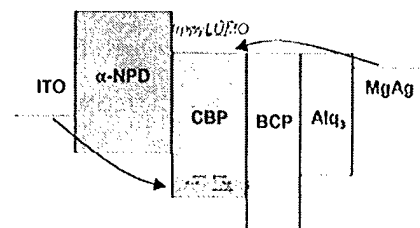
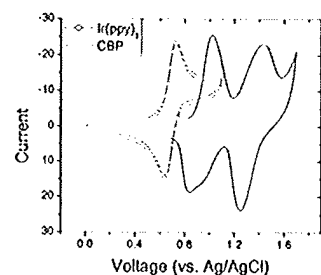
- All phosphors have $\tau < 5 \mu\text{sec}$
- Spectra constant on increasing bias/current

Dopant	peak η_{ext} (%)
Ir(bq) ₃	10
Ir(thpy) ₃	4 (unoptimized)



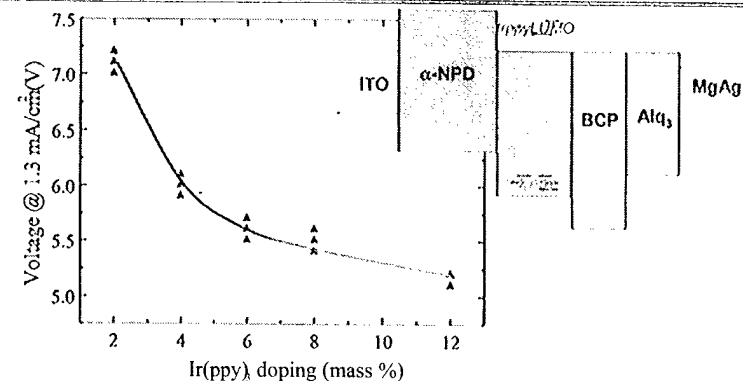
Ir(ppy)₃ traps holes in CBP

Cyclicvoltamograms of Ir(ppy)₃ and CBP



- Ir(ppy)₃ HOMO is 300 mV above the CBP HOMO
 - Same picture from both UPS and electrochemical measurements
- Ir(ppy)₃ reduction is 3 V above oxidation, *i.e.* Ir(ppy)₃ LUMO is above CBP
 - Y. Oshawa, *et. al.*, *J. Phys. Chem.*, 1987
 - Carrier gap (oxid. – red.) matches the ¹MLCT energy

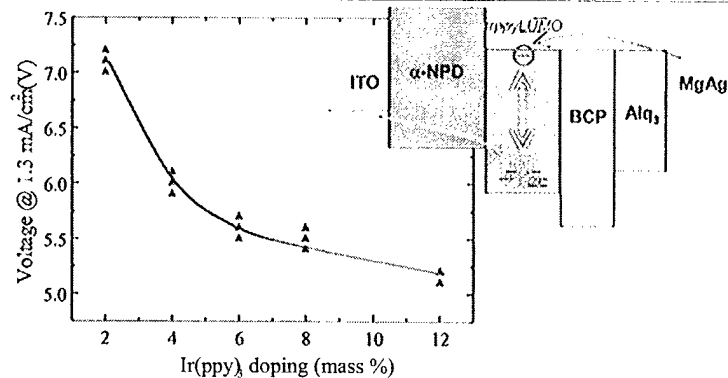
Conduction through Ir(ppy)₃ “trap” states



- Holes are carried by the Ir(ppy)₃ dopant at doping levels > 5%
- Hole leakage into Alq₃ will be dominant without hole blocker (BCP)
- All holes are localized on dopants, hole-electron recombination at the dopant
- Same Behavior is observed for other Ir based dopants (Ir(bq)₃ and ppy₂Ir(acac))

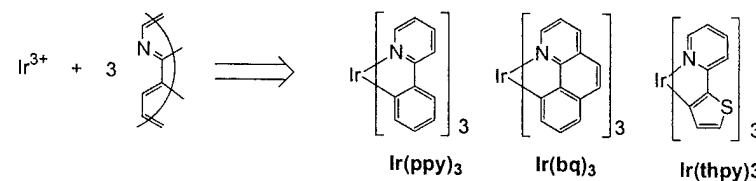
83

Conduction through Ir(ppy)₃ “trap” states

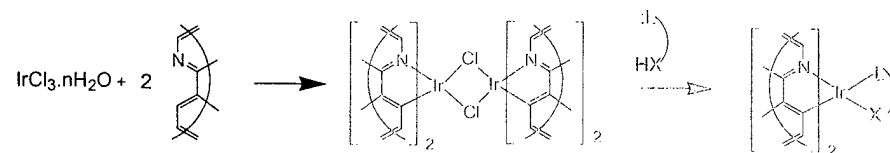


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Synthesis of Cyclometallated Ir Complexes

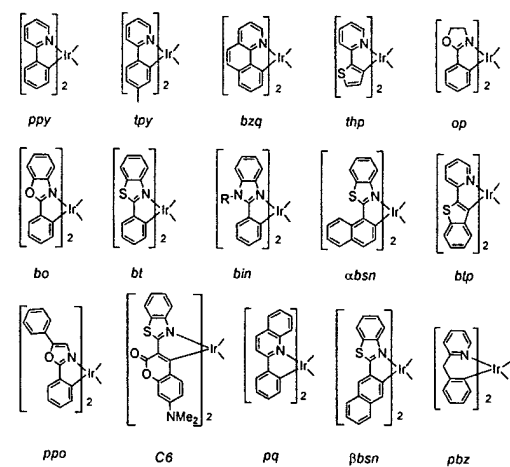


Reactions only work for ppy, bq and thpy ligands (and substituted derivatives)



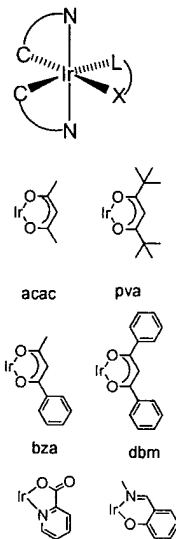
typical yield > 90%, similar yields for a wide variety of ligands
1st step: M. Nonoyama, *Bull. Chem. Soc. Jpn.* (1974)

Phosphorescent (C^N)₂Ir(LX) Complexes

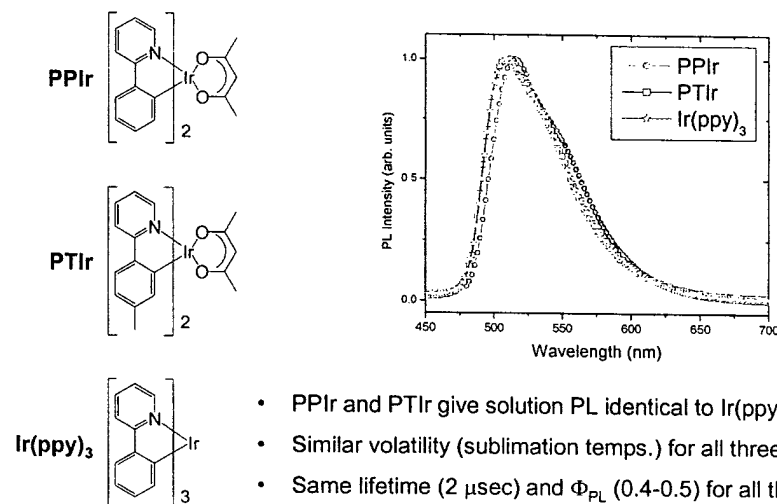


All acac cpds. emit with μsec lifetimes and $\phi_{PL} = 0.2-0.7$

S. Lamansky, et al., J. Am. Chem. Soc. (2001)



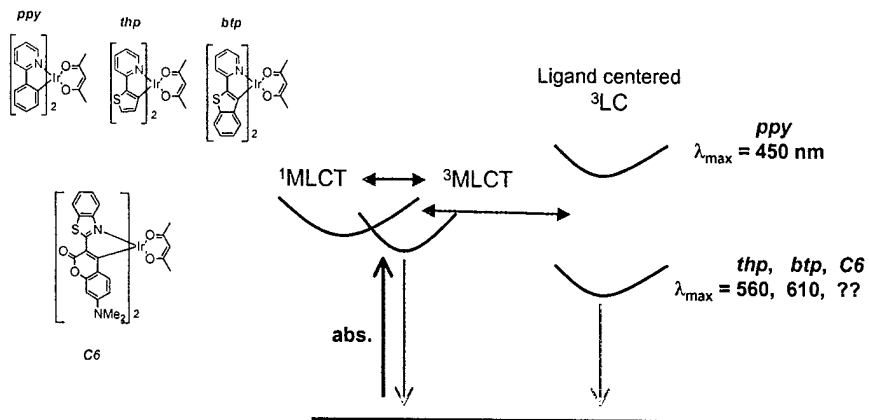
PL spectra of PPIr and PTIr



- PPIr and PTIr give solution PL identical to Ir(ppy)₃
- Similar volatility (sublimation temps.) for all three complexes
- Same lifetime (2 μsec) and Φ_{PL} (0.4-0.5) for all three

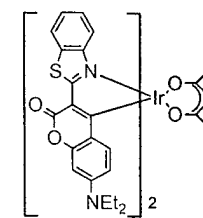
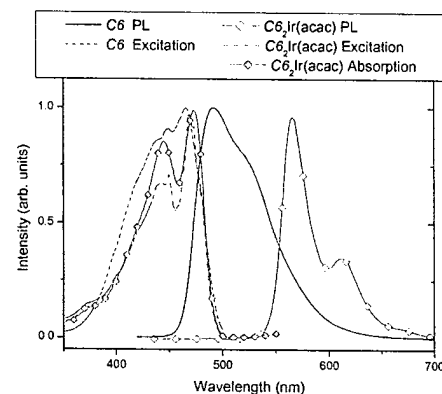
48

MLCT vs. LC excited states



- MLCT energy similar for ppy, thp, btp (450-475 nm).
- The choice of ³MLCT or ³LC emitting state depends on which is lower in energy
- Small Stokes shift is expected for MLCT emission.

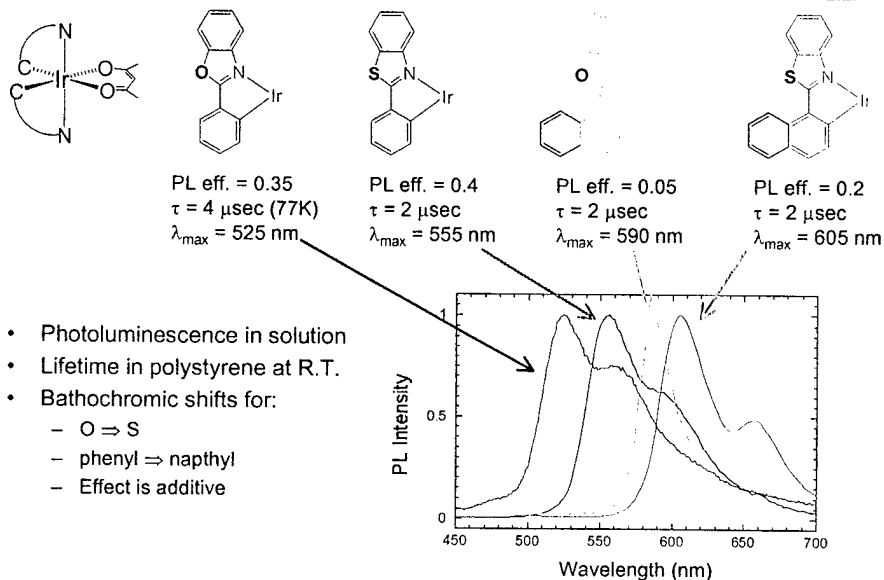
C₆Ir(acac) Excitation and Emission



C₆Ir(acac)
C₆ is shown in blue

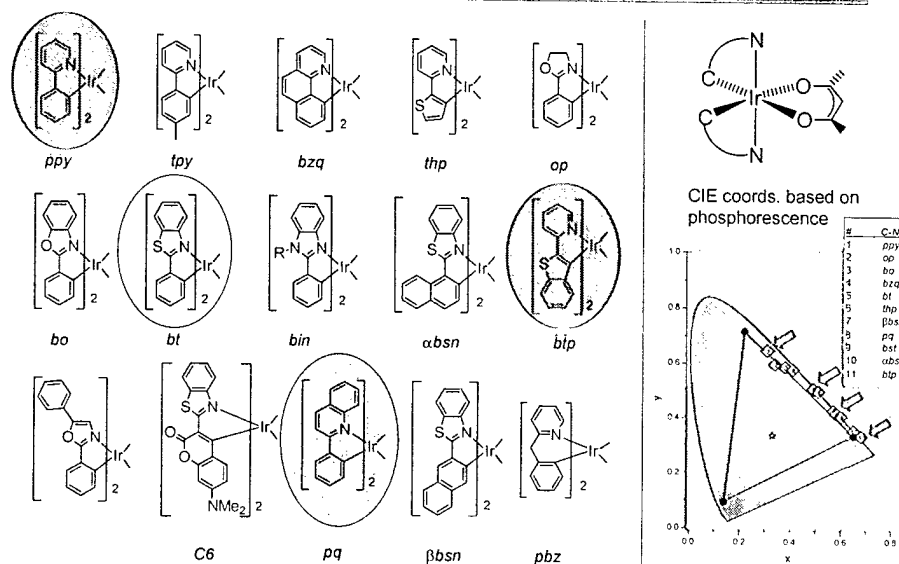
- Coumarin 6 (C₆) is a common green laser dye, used to fabricate green fluorescent OLEDs
- When this complex is cyclometallated to Ir the emission shifts to orange
 - Ir shifts dominant emission process to C₆ based phosphorescence
 - Excitation spectra of C₆Ir(acac) show lines for C₆ as well as MLCT transitions for "L₂IrX"
 - η (PL) for C₆Ir(acac) = 0.6 and τ = 14 μsec

Ligand Effects on Emission energy

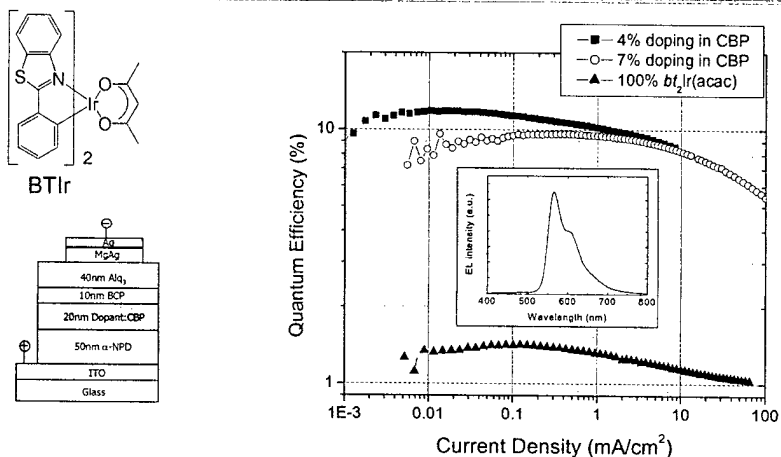


85

Green, yellow and red phosphors for OLED study

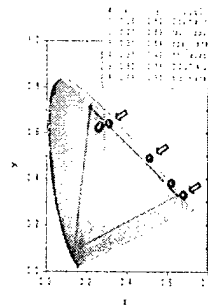


Performance of BTIr doped OLED (yellow emission)



- Peak external quantum Efficiency = 11%
- Efficiency with 100% BTIr emissive layer > 1.5%: very weak self quenching

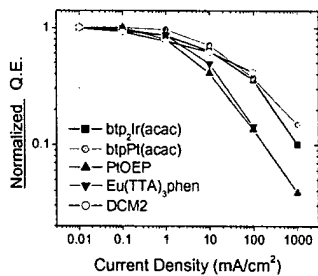
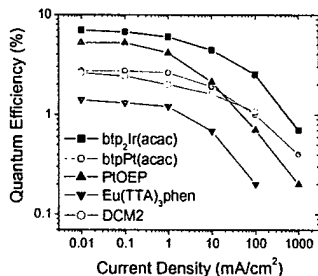
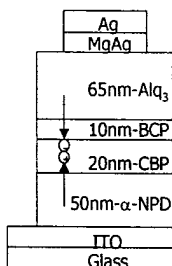
(C^N)₂Ir(acac) (C^N = ppy, bt and btp) doped (7%) OLED performance



C^N ligand	ppy	bt	btp
EL color	Green	Yellow	Red
Peak wavelength (nm)	525	565	617
Luminance @ 1 mA/cm^2 (cd/m^2)	441	300	62
Drive voltage (V) @ 1 mA/cm^2	7.2	7.3	8.5
Ext. quantum efficiency (%) @ 1 mA/cm^2	10.0	9.7	6.6
" @ 10 mA/cm^2	7.6	8.3	6.0
" @ 100 mA/cm^2	5.4	5.5	4.6
Power efficiency (lm/W) @ 1 mA/cm^2	18	11	2.2

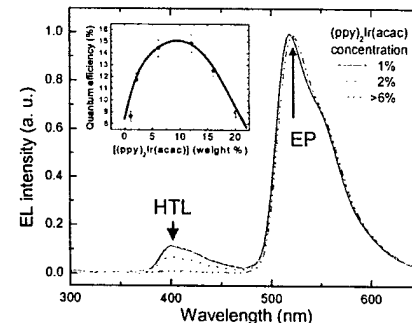
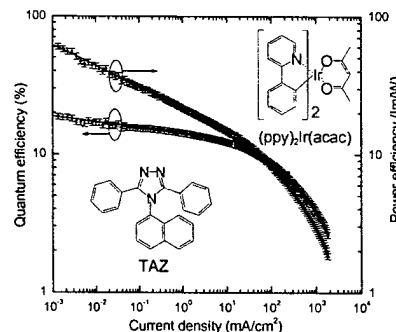
- Similar properties for PQIr (orange) OLED
- All dopants give external eff. > 11% for optimized structures (CBP host)
- Phosphors can be switched in a "modular" fashion with very little alteration of device performance

Saturated red OLEDs



- Doping concentration optimized for each dopant
- DCM2 device is not red, emission is yellow-orange (low doping concentration)
 - Fluorescence based device, NOT phosphorescence
- btp complexes of Ir give the best performance
 - Highest peak efficiency
 - Slowest drop off in eff. as a function of current density

Near 100% Efficiency

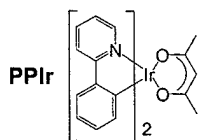
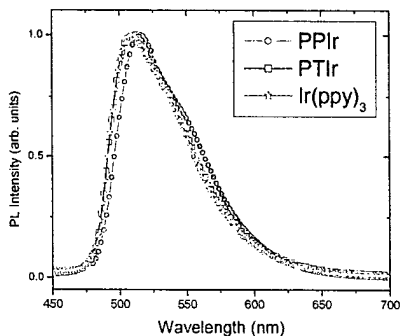
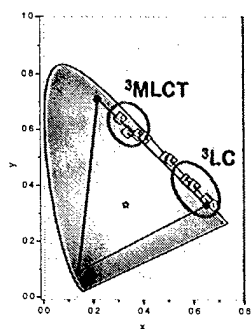


- Device structure: ITO/HTL/TAZ•(ppy)₂Ir(acac)/BCP/Alq₃/Li-Al
- Optimal doping concentration = 12%: high eff., low drive voltage
- $\eta_{ext} = (19 \pm 1)\%$, $\eta_{int} = (87 \pm 7)\%$, > 60 lum/W
 - $\eta_{ext} = 14\%$ at 1000 Cd/m² (2 mA/cm²)

S. Adachi, et. al., J. Appl. Phys., 2001

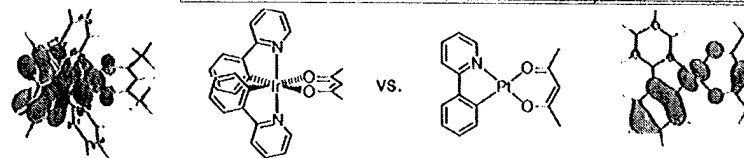
98

Green Emission from MLCT States

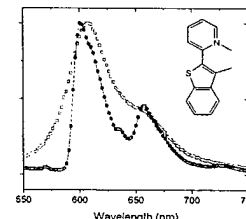
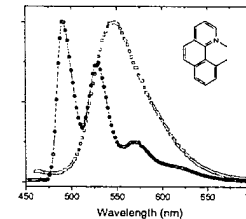
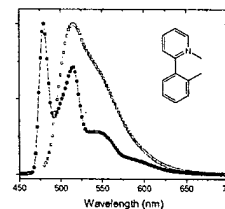


- Changes in C^N primarily affect ³LC, tune green → red
- Emission for ppy emitters results primarily from a metal centered transition, ³LC state for ppy $\lambda_{max} = 450$ nm
- Blue shifted MLCT ⇒ more ³LC character

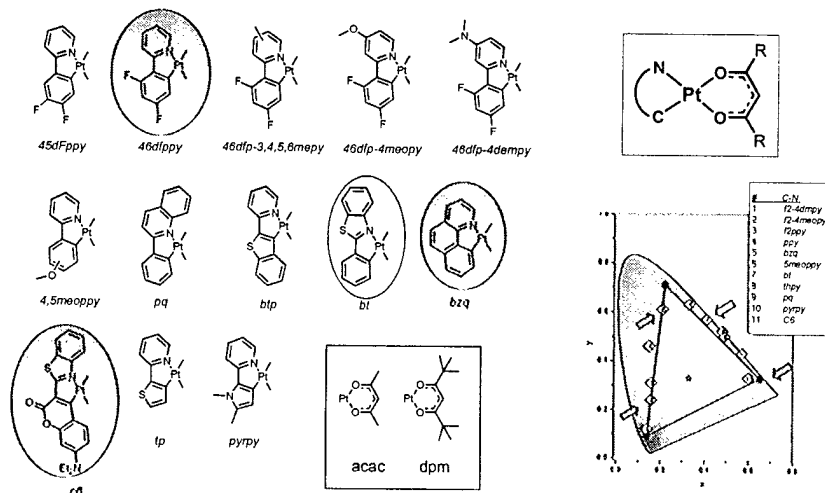
LPt(acac) Compared to L₂Ir(acac) Phosphors



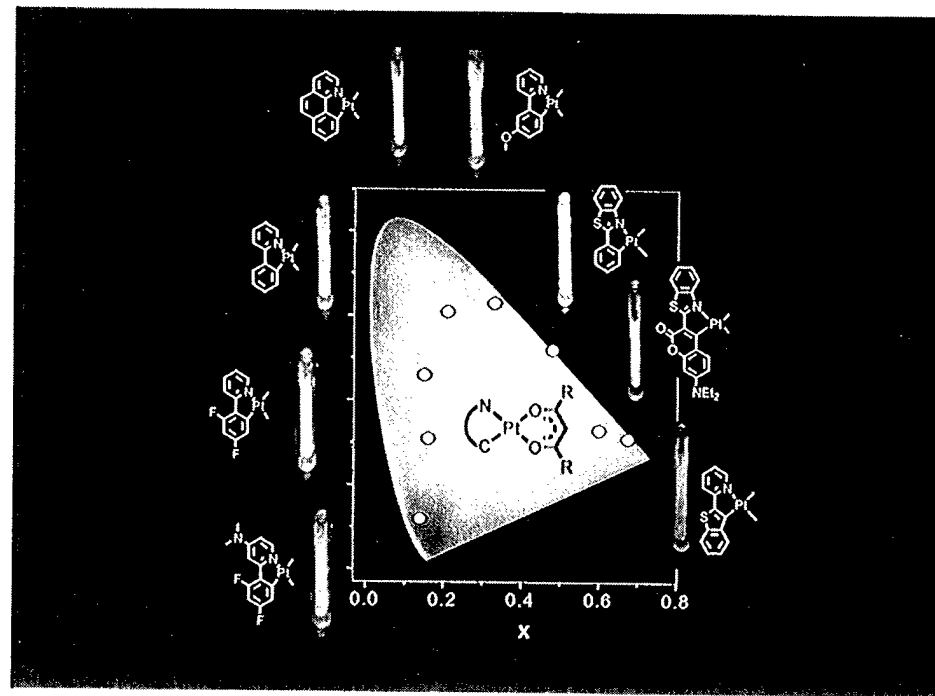
- MO pictures from DFT calculations, Spartan package
- Emission spectra LPt(acac) complexes are shown in blue and L₂Ir(acac) complexes in red.
- All LPt(acac) complexes have lifetimes of 5-10 μsec, $\phi_{PL} = 0.05-0.25$ (solution, 298K).
- Complexes with MLCT excited state show significant blue shift, L = ppy, bzq.



Cyclometalated Platinum Complexes

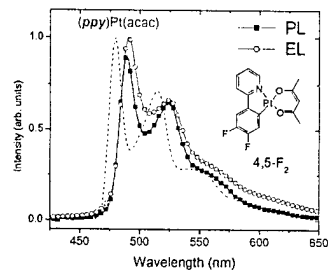


- Pt complexes have similar photophysics as the Ir analogs



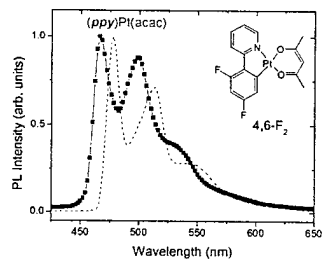
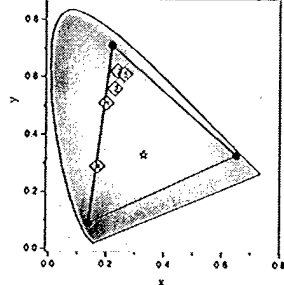
87

F₂-ppyPt(acac) PL and EL

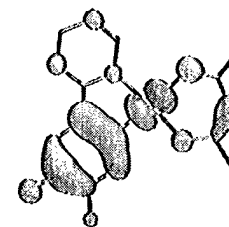
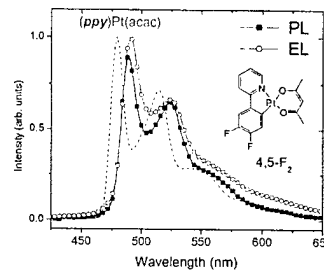


- PL and EL spectra nearly identical for 4,5-F₂-ppy
- 4,5- substitution gives red shift (rel. to ppy)
- 4,6- gives blue shift

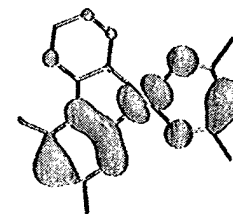
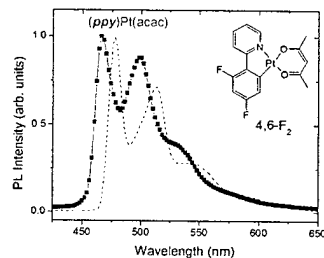
#	x	y	LPI(acac)
1	0.2	0.51	ppy
2	0.23	0.58	4,5-F ₂ ppy
3	0.24	0.62	4,5-F ₂ ppy - EL
4	0.17	0.29	4,6-F ₂ ppy
5	0.26	0.61	fac-Ir(ppy) ₃



F₂-ppyPt(acac) PL and EL

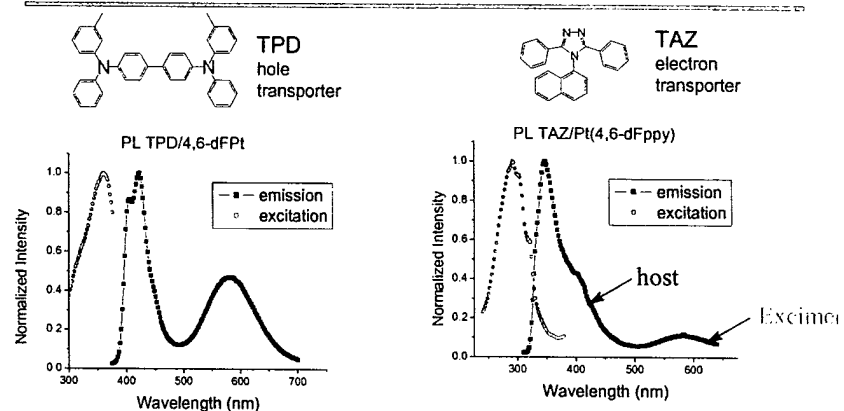


Weak π donation
para to Pt raises
HOMO: red shift

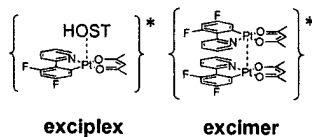


Inductive e⁻ withdrawal
meta to Pt lowers the
HOMO: blue shift

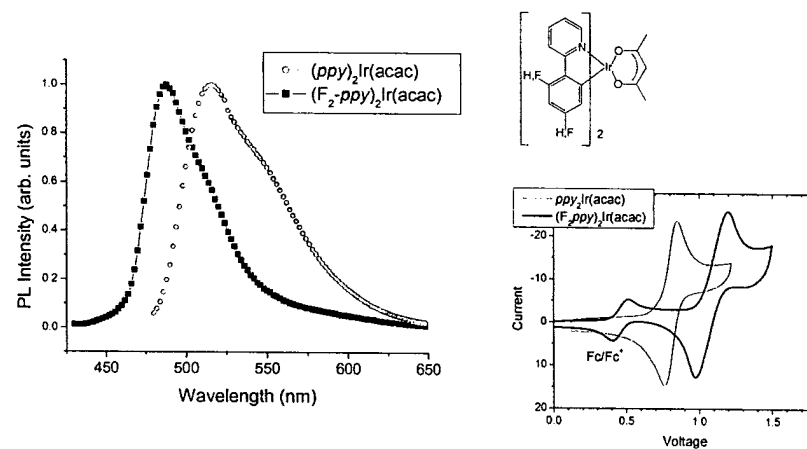
PL of Pt(4,6-dFppy)(acac) in OLED host materials



- TPD is a common HTL, TAZ is a common ETL
- Only TAZ/TPD and excimer (580 nm) emission in both hosts
- Identical red emission in both HTL and ETL suggests excimer and not exciplex



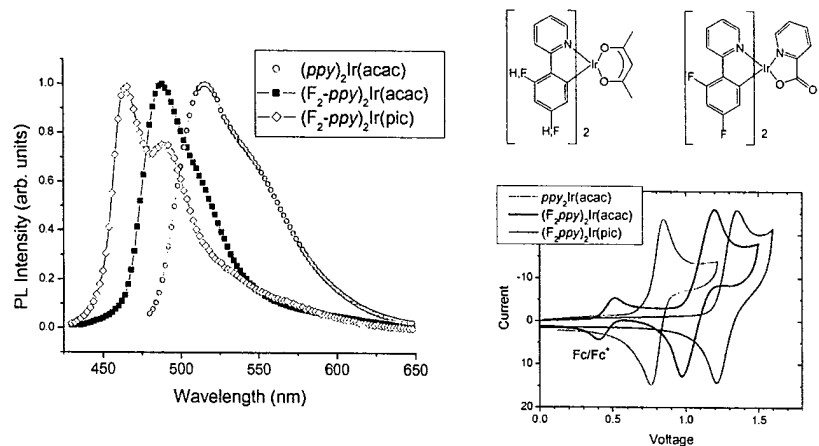
(4,6-F₂-ppy)₂Ir(acac) solution PL/electrochemistry



- Octahedral center \Rightarrow decrease exciplex formation
- F substitution leads to lowering HOMO, and blue shift in emission (MLCT)
 - 275 mV shift in the oxidation potential
 - 140 mV blue shift in emission

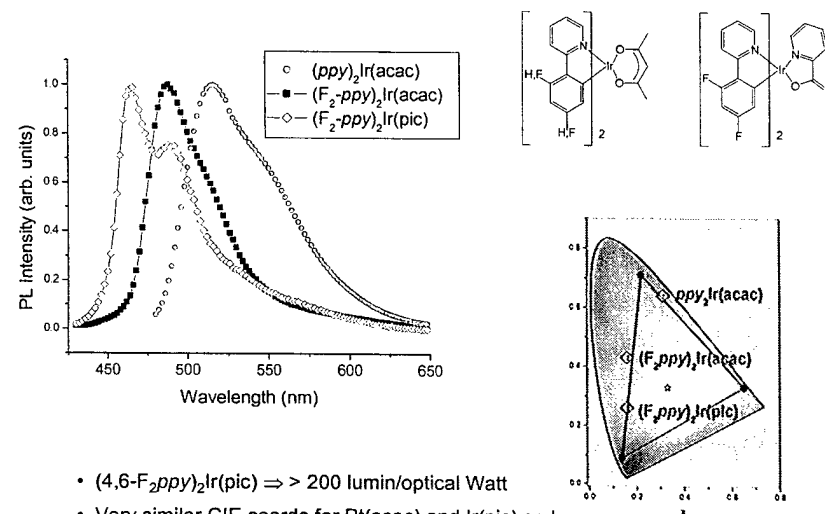
88

(4,6-F₂-ppy)₂Ir(LX) solution PL/electrochemistry



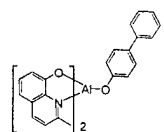
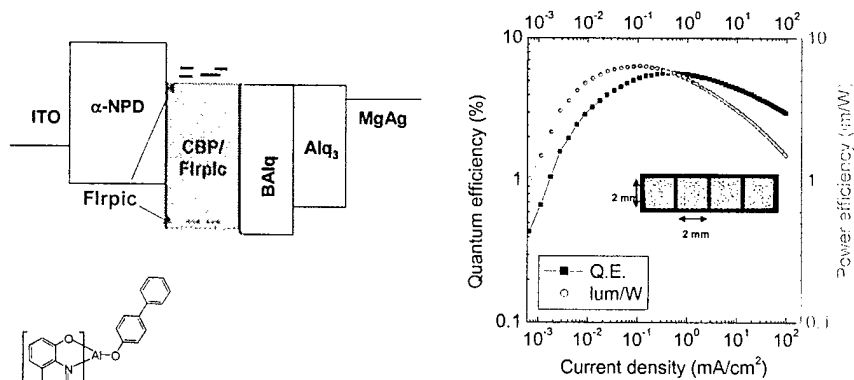
- pic substitution leads to further lowering HOMO, and blue shift in emission
 - 475 mV shift in the oxidation potential
 - 275 mV blue shift in emission
- Emission spectrum consistent with MLCT + $^3\pi-\pi^*$

(4,6-F₂-ppy)₂Ir(LX) solution PL/electrochemistry



- (4,6-F₂ppy)₂Ir(pic) \Rightarrow > 200 lumin/optical Watt
- Very similar CIE coords for Pt(acac) and Ir(pic) cpds.
- Octahedral center should decrease excimer/exciplex formation

Blue Electrophosphorescence from FIrpic/CBP

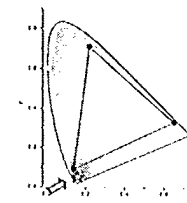
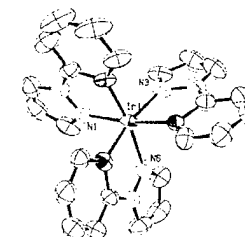
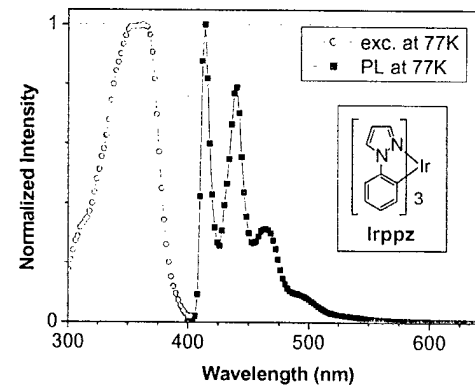


BAQ

- Emission due solely to phosphorescent dopant
 - No excimer or exciplex
- FIrpic carries electrons in CBP
- Efficiency = 5.5%, > 5 lum/W, 12 cd/A at 100 cd/m²

C. Adachi, et. al., *Appl. Phys. Lett.* (2001)

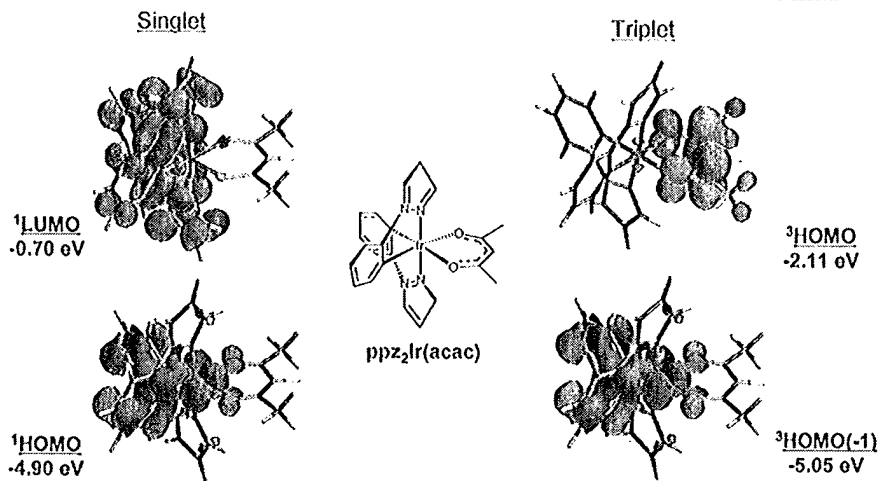
Tris(1-phenylpyrazole) Iridium Complexes



- ppz ligand has high triplet energy
- No luminescence at room temperature
- Are ppzIr derivatives inherently weak emitters?

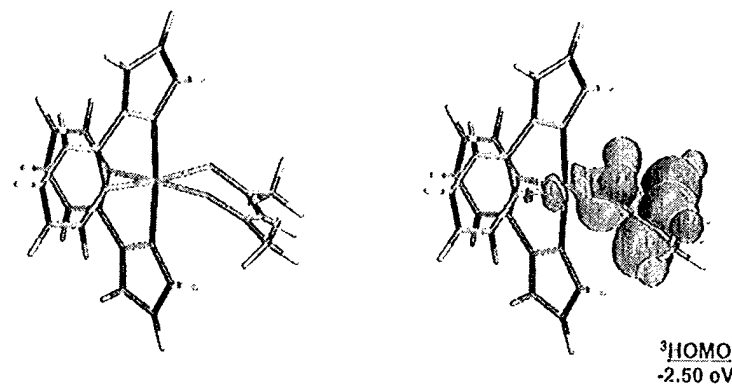
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ppz₂Ir(acac) Valence MOs



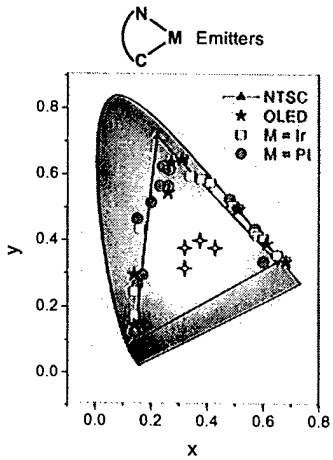
- Triplet is a charge separated state

Minimized Triplet Geometry for ppz₂Ir(acac)



- Estimated triplet energy gap:
 - $\Delta E(\text{singlet-triplet}) \approx 2.40 \text{ eV}$ (517 nm) [520 nm, expt.]
- Significant geometry changes in the excited state \Rightarrow quenching
- LX ligands with higher triplet energies are needed to prevent quenching

Summary



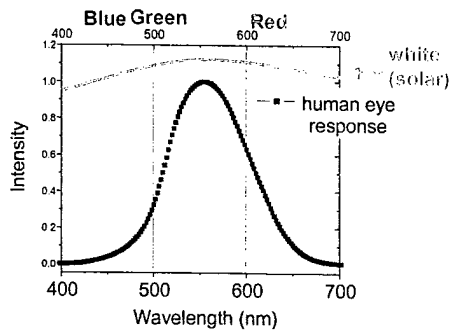
- Careful control of the formation, confinement and relaxation of excitons can lead to highly efficient OLEDs
 - Metals are good, expensive metals are better
 - Both carrier and exciton trapping at the phosphor are critical for high efficiency
 - Using Ir based phosphors we have demonstrated $\eta_{int} > 90\%$ for green, $> 60\%$ for red, yellow and orange and $> 25\%$ for blue
 - Lifetimes for green, orange and red devices $> 50,000$ hours
- Careful design of ligands in Ir and Pt complexes leads to efficient, highly tunable phosphors for OLEDs
 - Control of the excited state
 - High efficiency regardless of color (blue, green, yellow, red)
 - Blue \rightarrow Red and White

06

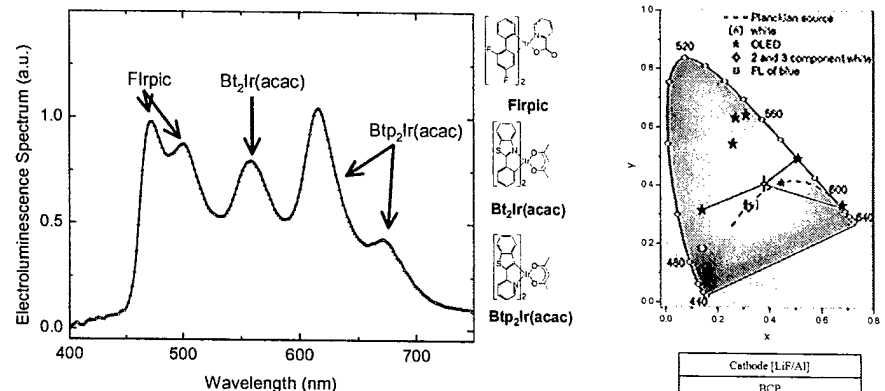
Color Mixing to Achieve White Emission

- You need a broad spectrum for good white illumination
- Color mixing with different colored OLEDs
 - Side-by-side arrangement of RGB elements, similar to flat panel display
 - Short R, G and B pixels together
 - Transparent devices can be stacked
 - Pixels on top of pixels with a common substrate
 - Large sheets of transparent R, G and B OLEDs can be stacked to achieve white

- Different dyes can be doped into emissive layer(s) of the OLED
 - multiple dopants in a single layer lead to complications due to energy transfer
 - segregate dopants into separate layers
 - How many emitters are needed?



Three phosphor white OLEDs: Each phosphor in a separate layer



- CIE coordinates = 0.37, 0.40, $\eta_{ext} = 5.2\%$
- maximum luminance = 31 000 cd/m²
- CRI = 83

B. D'Andrade, et. al., *Advanced Materials* (2001)

Acknowledgements

Jason Brooks, Vadim Adamovich, Peter Djurovich, Arnold Tamayo, Jian Li, Drew Murphy, Liza Babayan, Sergey Lamansky, Douglas Loy, Yujian You
Chemistry, University of Southern California

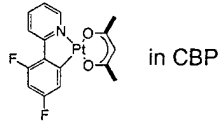
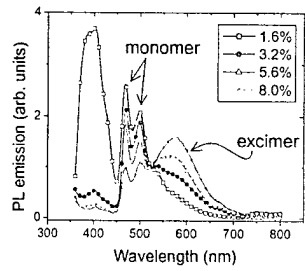
Stephen Forrest, Brian D'Andrade, Marc Baldo, Paul Burrows
 Diarmid O'Brien Chihaya Adachi
Electrical Engineering, Princeton University

Raymond Kwong, Mike Weaver, Julie Brown
Universal Display Corporation

\$\$ Funding: Universal Display Corporation, NSF, DARPA

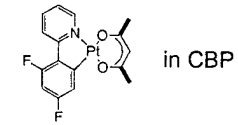
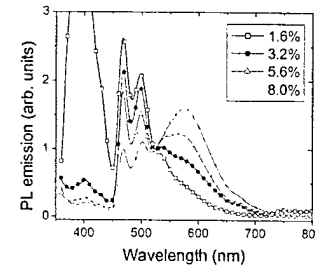
Cathode (LiF/Al)
BCP
3 wt% Btp ₂ Ir(acac):CBP
6 wt% Firpic:CBP
NPD
PEDOT:PSS
ITO
Substrate (Glass)

Single Dopant Monomer – Excimer Photoluminescence

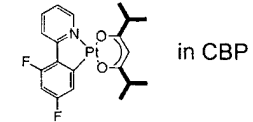
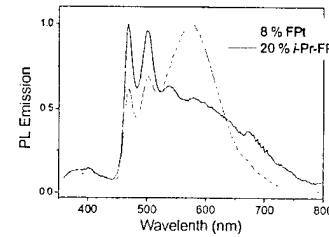


- monomer dopant emission at low doping level
- balanced monomer/excimer ca 5%
- CBP fluorescence at low doping levels
- Increasing steric bulk can hinder excimer formation
 - could it lead to greater monomer:excimer ratio?

Single Dopant Monomer – Excimer Photoluminescence



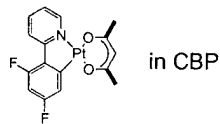
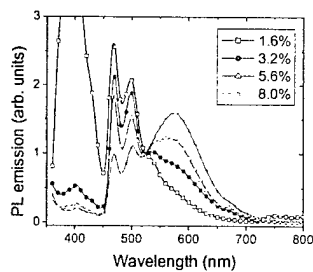
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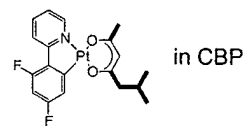
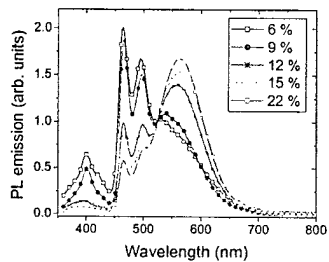
- replacing the methyl groups of FPT with *i*-Pr adds significant steric bulk
- Only weak excimer emission is observed at doping levels as high as 20%
- too much steric bulk gives only monomer, we need intermediate steric bulk.

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Single Dopant Monomer – Excimer Photoluminescence

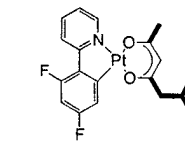


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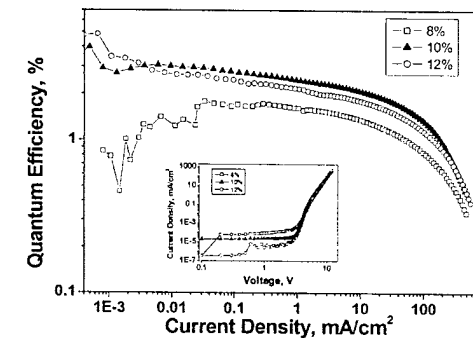
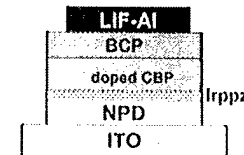


- Now FPT has one methyl and one butyl
- Excimer emission is now observed, and balanced monomer:excimer is seen between 9 and 12%, an ideal doping level for OLEDs

High Efficiency Single Dopant WOLEDs

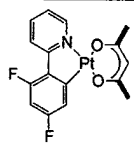


- doped luminescent layer
- only 4 organic layers and one dopant

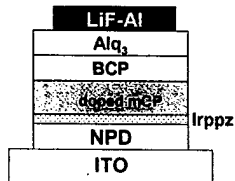


Transfer is still endothermic

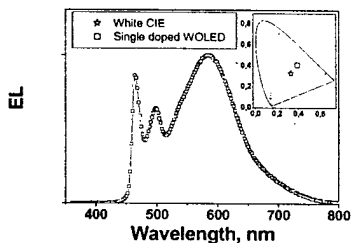
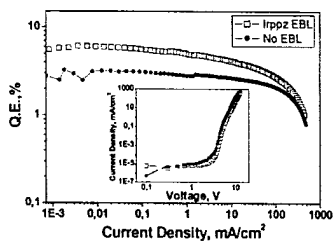
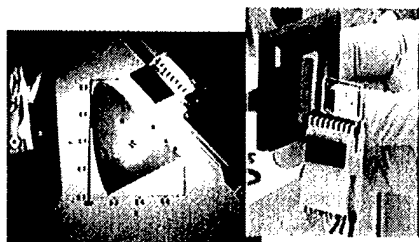
High Efficiency Single Dopant WOLEDs



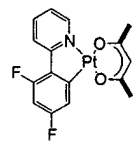
• doped mCP layer



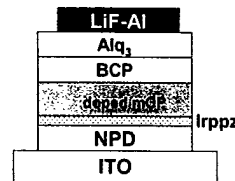
no Irppz: low eff. and NPD emission contribution



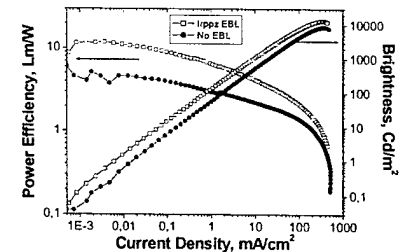
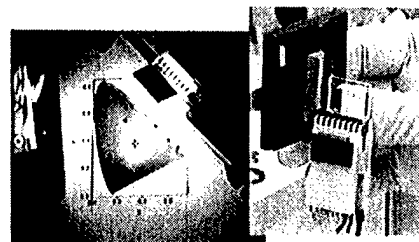
High Efficiency Single Dopant WOLEDs



• doped mCP layer



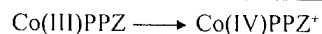
no Irppz: low eff. and NPD emission contribution



- Q.E = 6% , 12 lum/W @ 1 cd/m²
- Q.E = 4.5% , 5.1 lum/W @ 500 cd/m²

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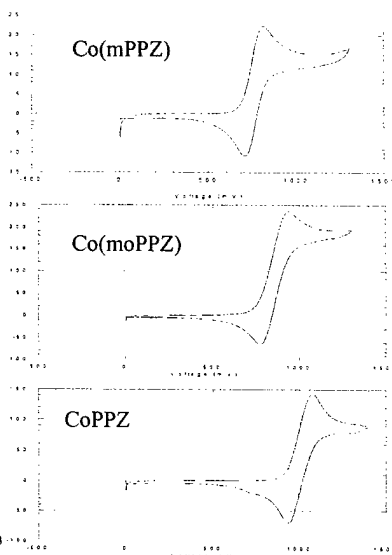
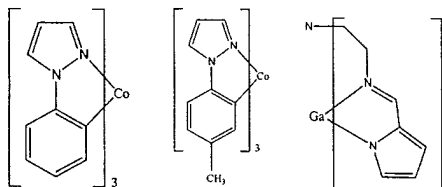
Cyclic Voltammetry and Ultraviolet Photoemission Data



The electron-rich phenylpyrazole ligand stabilizes the Co(IV) species produced electrochemically.

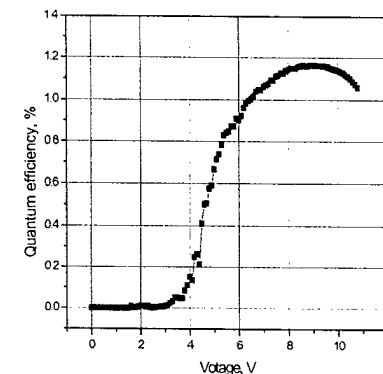
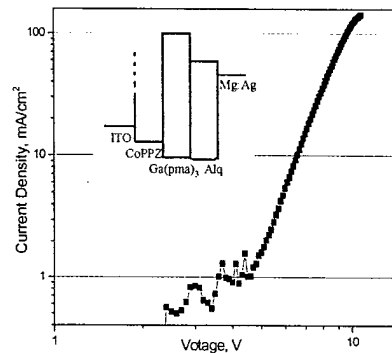
UPS Data (HOMO)

- CoPPZ: 5.37eV
- Co(mPPZ): 5.38eV
- NPD: 5.51eV
- Gap_{ma}: 5.74eV



Efficient OLED with ONLY Metal Complexes(1)

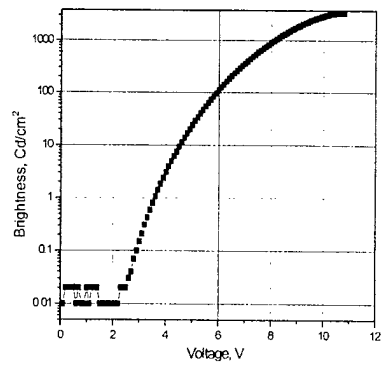
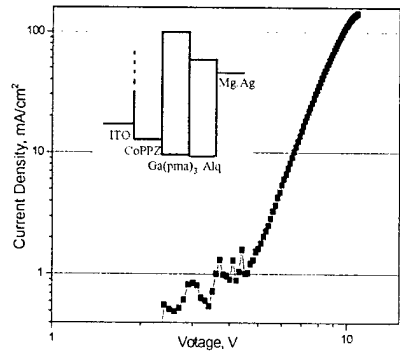
ITO/Coppz(400Å)/GaPMAEA(100Å)/Alq(500Å)/Mg:Ag(1000Å)/Ag(400Å)



Unfortunately, the device lifetime is poor with a Coppz HTL.

Efficient OLED with ONLY Metal Complexes(1)

ITO/Coppz(400Å)/GaPMAEA(100Å)/Alq(500Å)/Mg:Ag(1000Å)/Ag(400Å)



DARPA HDS Final Program Review

5-3-02

Julie Brown

jjbrown@universaldisplay.com

Universal Display Corporation

HDS UDC Program Objectives

- Demonstrate Reliability
- Fabricate Engineering Prototypes
- Design Pilot Line Facility

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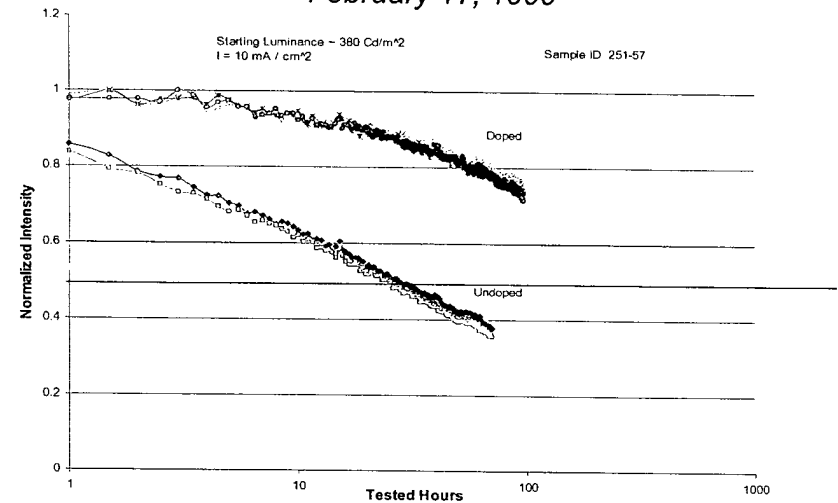
Program Elements

- Reliability Task
 - » Life Test System
 - » Process and Packaging
 - » Phosphorescent OLEDs
- Display Prototype Task
 - » Passive Matrix Design
 - » TOLED Passive Matrix Prototype
 - » FOLED Passive Matrix Prototype
 - » Active Matrix Display Prototype
- Pilot Line Facility

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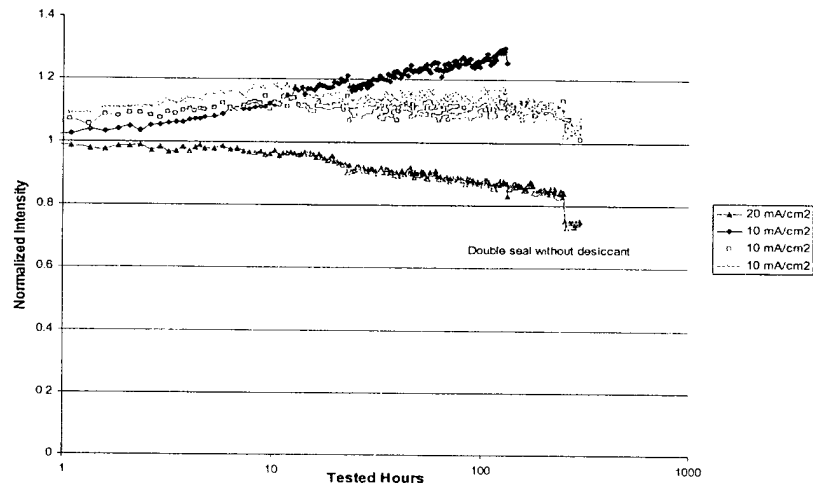
OLED Lifetime: Doped vs Undoped - February 17, 1999 -



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Red PHOLED Preliminary Data

- February 17, 1999 -



Optimization of Electrophosphorescent Devices

- Efficiency
- Device stability
- Color purity



Substrate: surface treatment
 Material: hosts, dopants, transporters, blockers, cathode materials
 Purity: synthesis, purification
 Structure: device architecture, layer thickness, doping concentration
 Encapsulation: sealants, getters, curing method
 Testing: hardware, software

Red Phosphorescent OLED Lifetime

- April 19, 2000 -

- Device Design

Sample A:

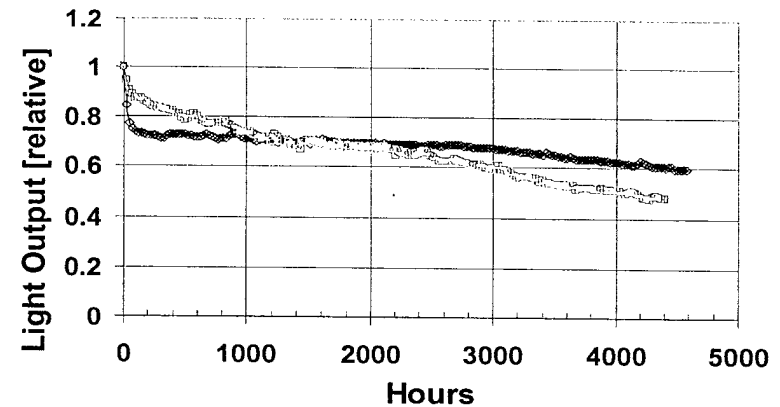
ITO(1500A)/CuPc(200A)/NPD(400A)/CBP:PtOEP(300A)/
 Alq₃(200A)/Mg:Ag

Sample B:

ITO(1500A)/CuPc(200A)/NPD(400A)/Alq₃:PtOEP(300A)/
 Alq₃(200A)/Mg:Ag

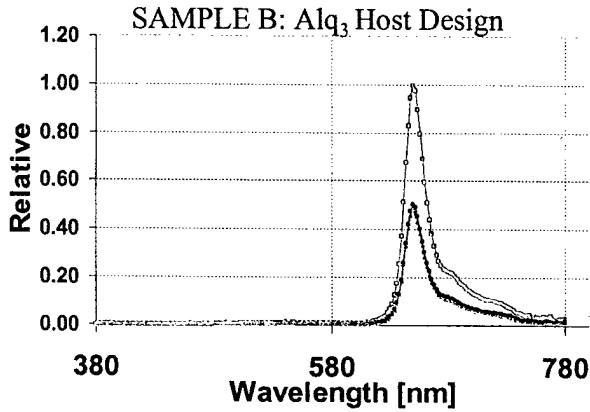
Study of Lifetime Dependence on Phosphor Host

Red PHOLED Operational Stability



Alq₃ Host: Lifetime (50%) = 4000 hours
 CBP Host: Lifetime(50%) = 8000 hours

Red OLED Spectral Response Stability

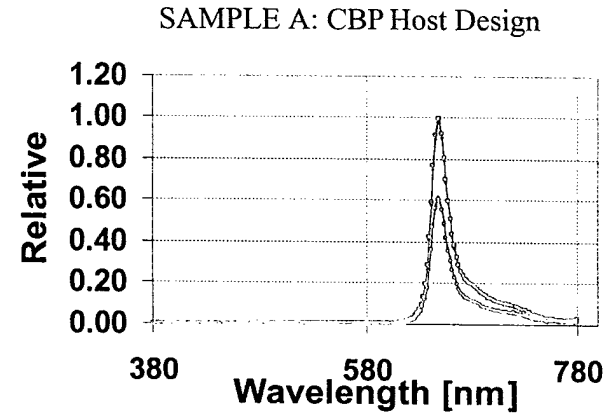


Comparison of response: t=0 and t=4500 hours

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April 19, 2000

Red PHOLED Spectral Response Stability



Comparison of response: t=0 and t=4500 hours

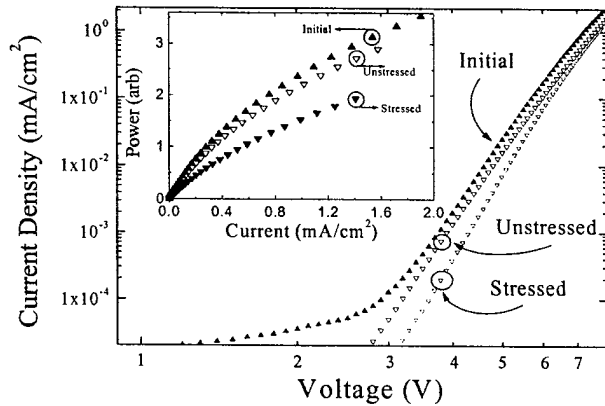
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April 19, 2000

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Red OLED LIV Stability

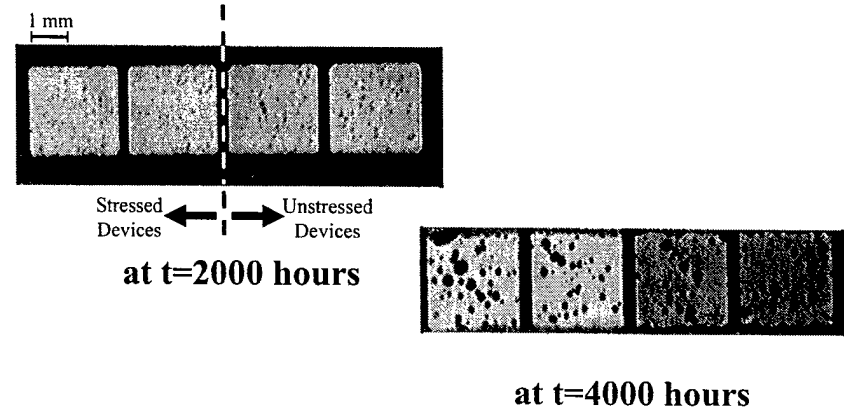
Sample A: CBP Host



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April 19, 2000

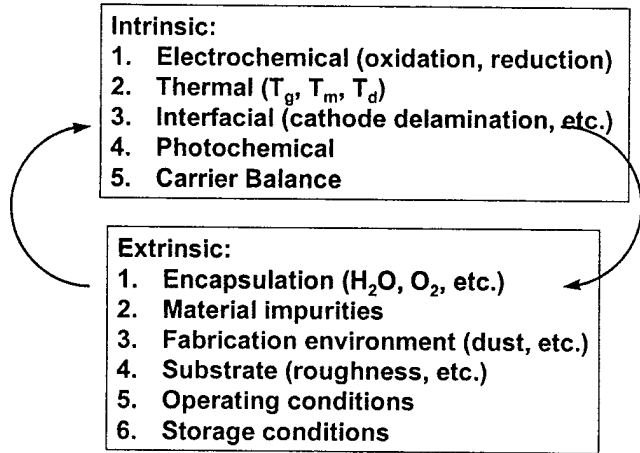
Red PHOLED Package Failure



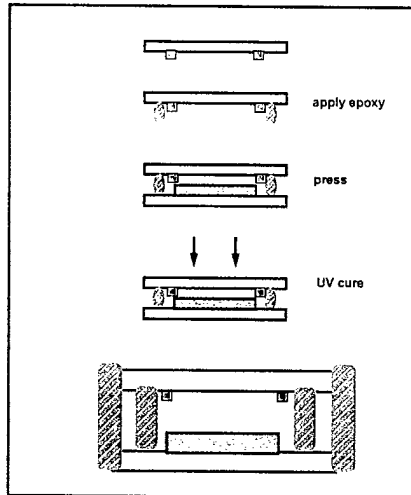
UNIVERSAL DISPLAY CORPORATION

April 19, 2000

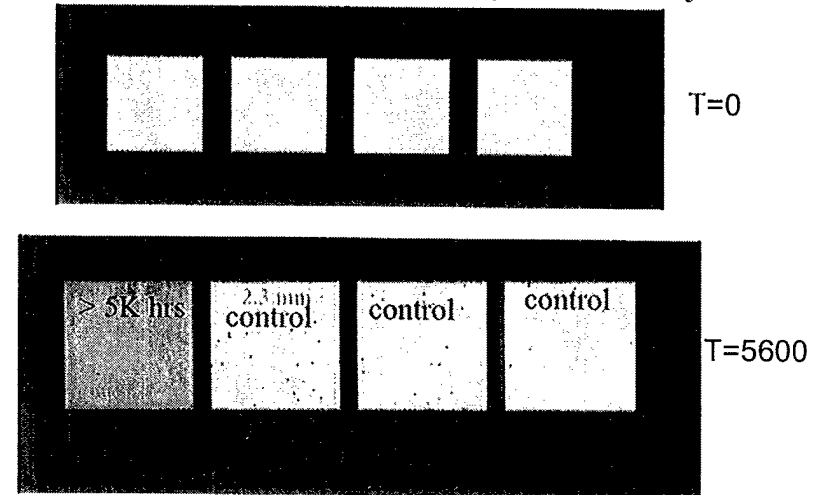
Device Stability Interacting Factors

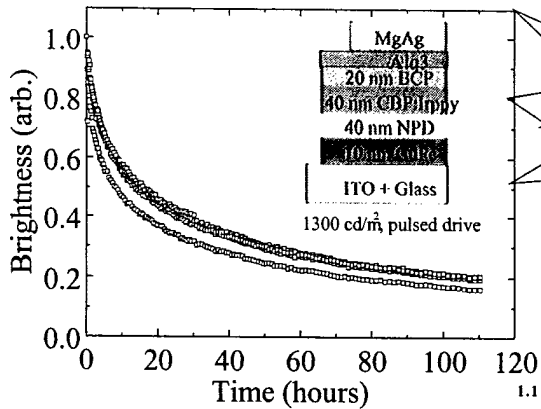


Encapsulation Process Flow



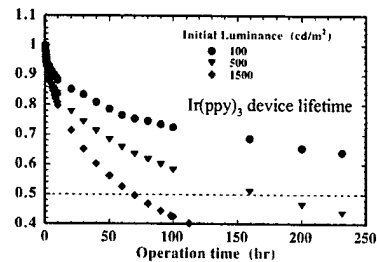
Green PHOLED Package Stability





Are Green Phosphors Stable?

Also, Tsutsui et al. Jpn. J. Appl. Phys. 38 in press...



BCP Crystallization?
Phosphor Degradation?

Hole Blocking Materials

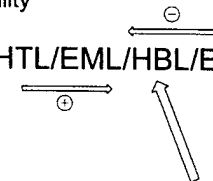
Basic requirements:

- Hole blocking (low HOMO level) and/or low hole mobility
- Electron transporting
- No quenching of the dopant emission

Stability issue:

1. Anion stability
2. Thermal stability

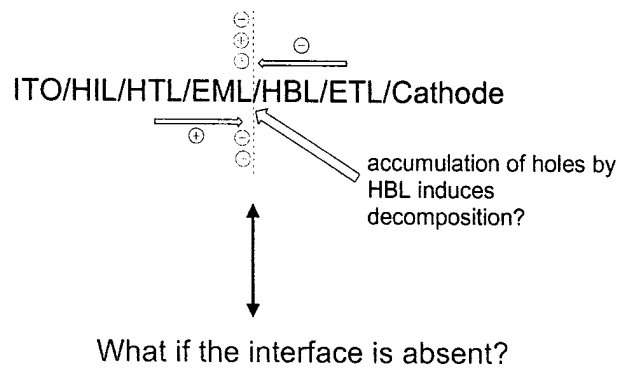
ITO/HIL/HTL/EML/HBL/ETL/Cathode



what is the anion stability?
what is the morphological stability?

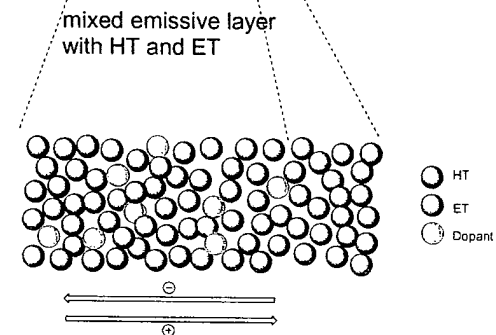
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OLED Design For Long Lifetime



Mixed Layer Devices

General structure:
ITO/HIL/HT:ET:Dopant/ET/Cathode

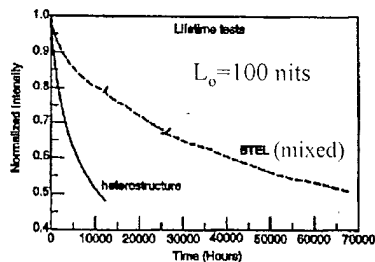


Largely reduced charge accumulation

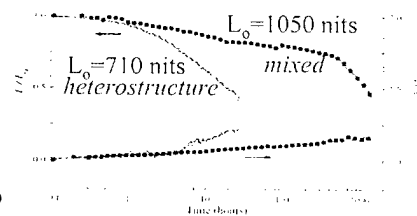
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Previous Mixed Layer Work



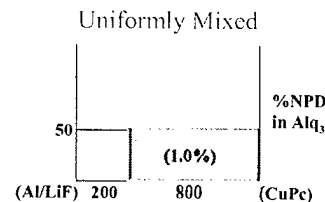
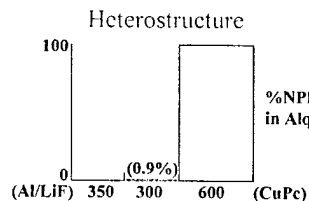
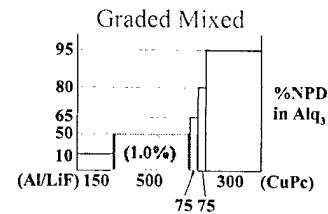
Choong et al., *APL* 75(2), 172 (1999)



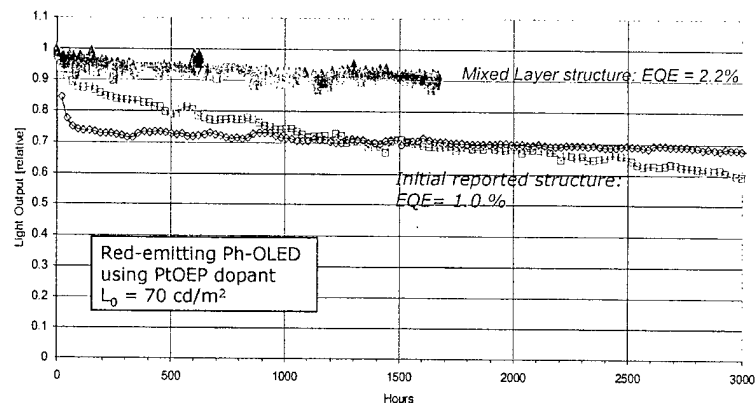
Aziz et al., *Science* 283, 1900 (1999)

- Naka et al., *Jpn. J. Appl. Phys.* 33, L1772 (1994)
- Kido et al., *APL* 67, 2281 (1995)
- Wen et al., *APL* 71, 1302 (1997)

Device Structures- Current Study



Lifetime Comparison of Deep Red PHOLEDs



Mixed Layer PHOLED Lifetime Extrapolates to > 10⁶ hours

Device Structures

Three basic device structures were employed in this study. The data presented correspond to the following structures, which contain a fluorescent green dopant (D):

■ Heterostructure

Al
LiF
Alq ₃
Alq ₃ :D (0.9%)
α-NPD
CuPc
ITO

▣ Graded Mixed

Al
LiF
α-NPD:Alq ₃ (90%)
α-NPD:Alq ₃ :D ((1:1):1.0%)*
α-NPD:Alq ₃ (35%)
α-NPD:Alq ₃ (20%)
α-NPD:Alq ₃ (5%)
CuPc
ITO

▲ Uniformly Mixed†

Al
LiF
α-NPD:Alq ₃ (1:1)
α-NPD:Alq ₃ :D ((1:1):1.0%)
CuPc
ITO

*NPD:Alq₃=1:1 unless otherwise noted

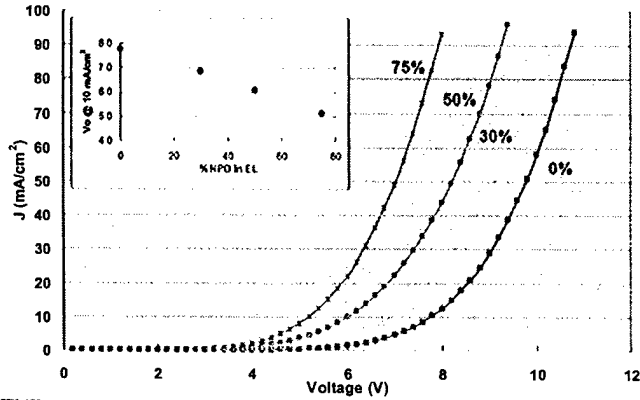
†V-E. Choong et al., *APL* (1999), 75(2), 172

For comparative purposes, the properties of a device with a phosphorescent green dopant are also presented:



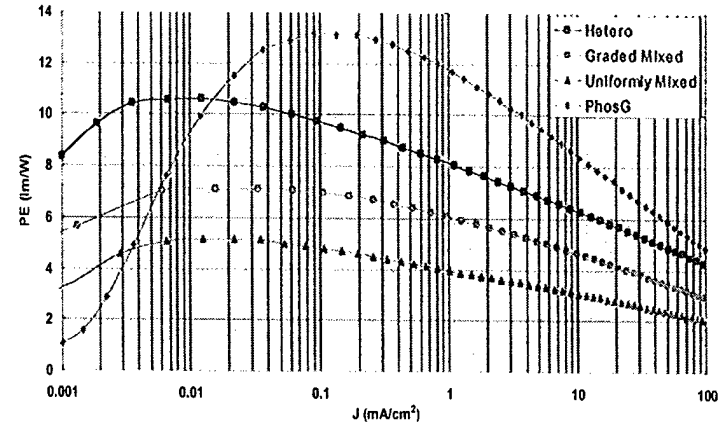
J-V and V_0 Comparison

The dependence of the J-V characteristics on percentage of NPD in the emissive layer of the graded mixed devices is shown below (0% corresponds to the heterostructure). The inset illustrates the decrease in driving voltage V_0 with increasing %NPD.



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Power Efficiency Comparison

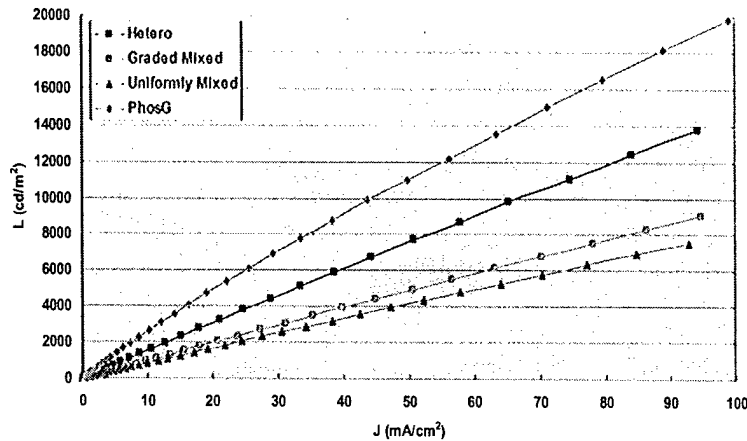


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Performance Comparison

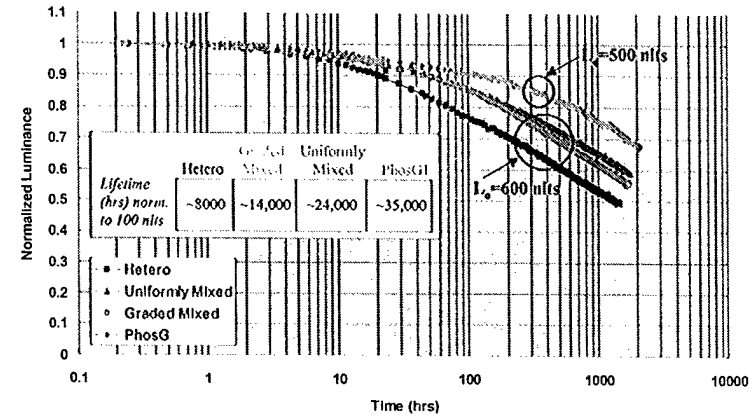
Luminance vs. current density of the fluorescent and phosphorescent OLEDs:



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Device Lifetime

The lifetime data (DC, constant current) show that mixing the HT and ET layers improves the lifetime of the device.

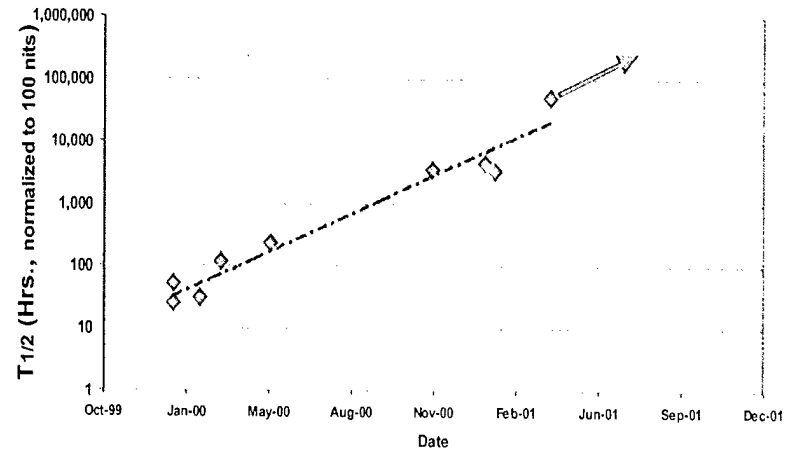


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Data Summary

	Hetero	Graded Mixed	Uniformly Mixed	PhosG
Power Efficiency (lm/W) @ 100 nits	8.4	6.0	3.8	12.7
Driving Voltage (V) @ 100 nits	5.5	4.5	5.9	6.4
Lifetime (hrs) Normalized to $L_0=100$ nits (DC, const. J)	~8000	~14,000	~24,000	~35,000

Green PHOLED Lifetime Progress

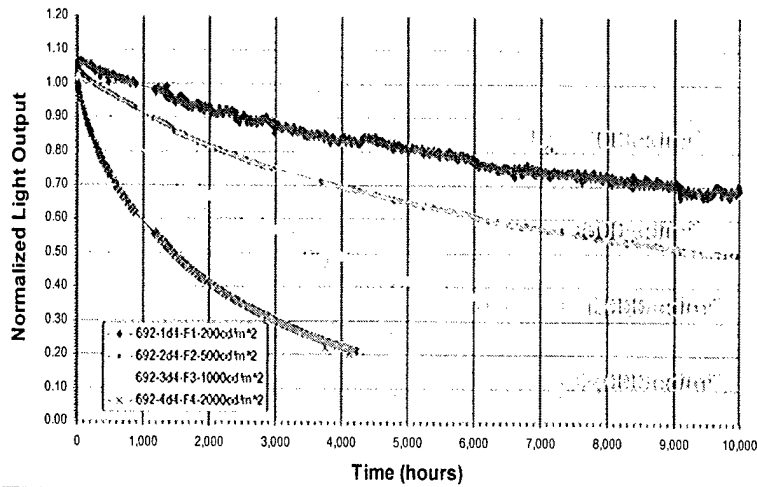


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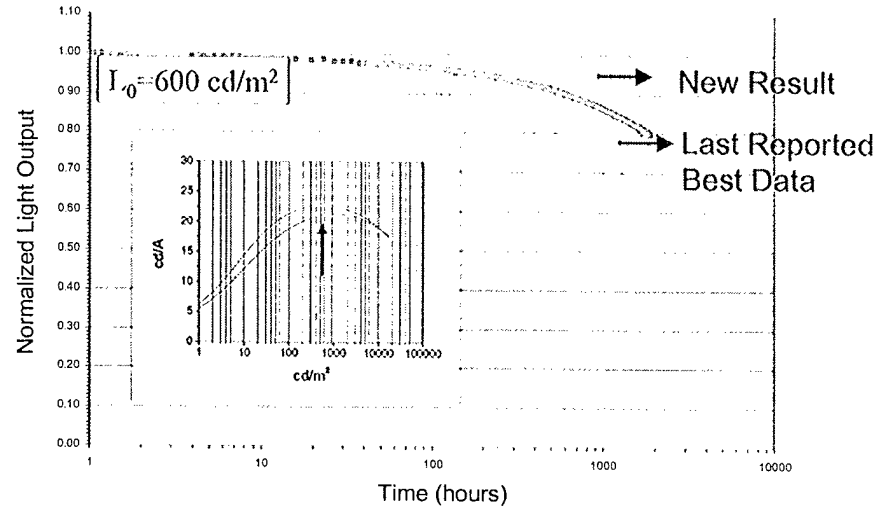
101

Green PHOLED Lifetime



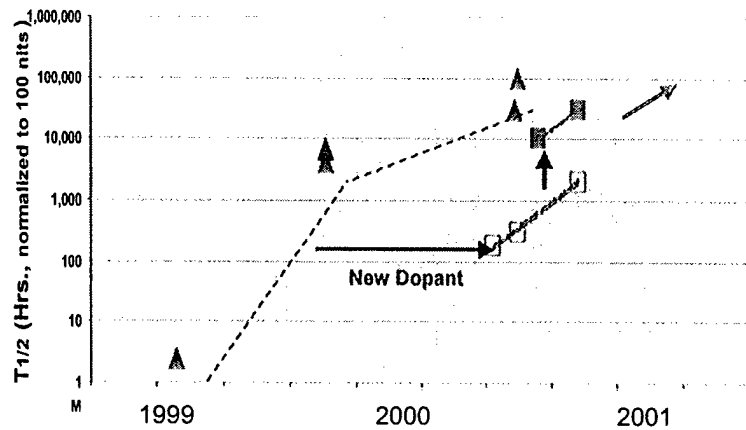
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Green PHOLED New Results



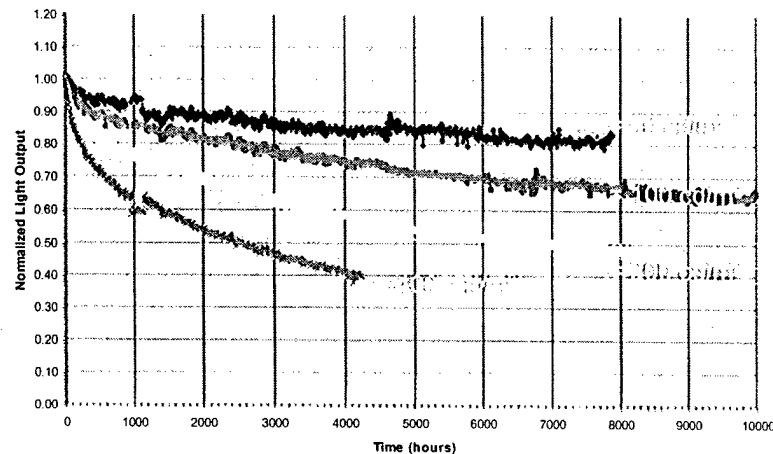
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Red PHOLED Lifetime Progress



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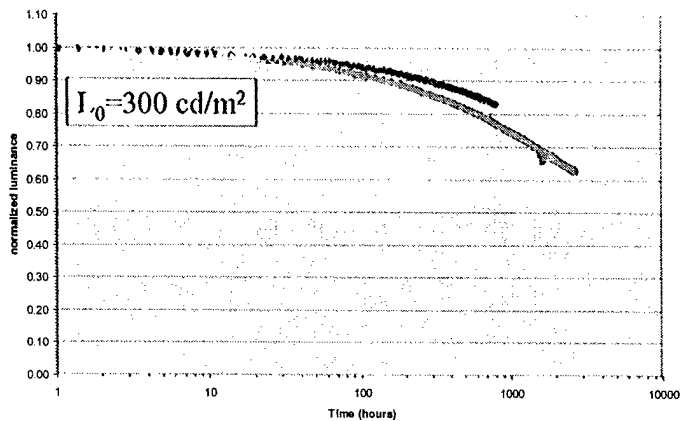
Mixed Layer Red PHOLED Lifetime



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RED PHOLED Lifetime New Results

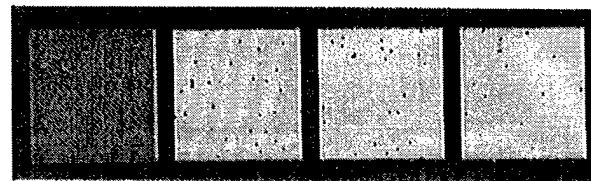
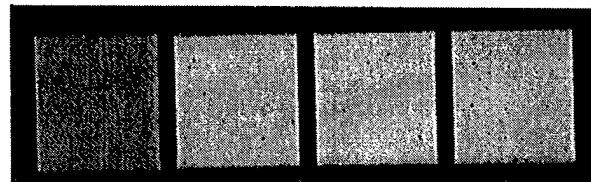


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Red and Green PHOLEDs

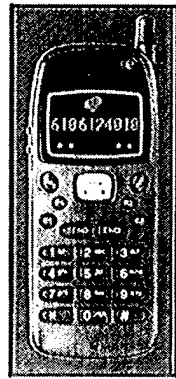
t = 10,000 hours actual test time

May 1, 2002



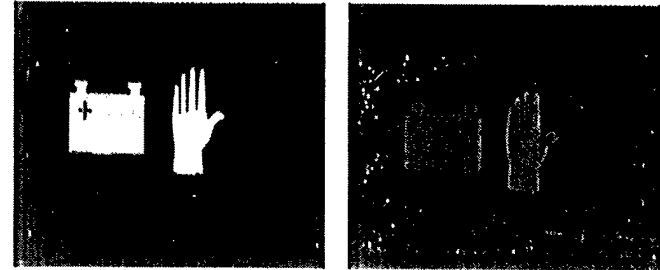
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Early Static OLED Prototype



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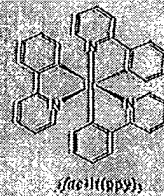
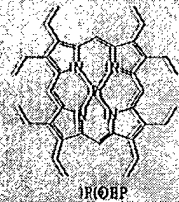
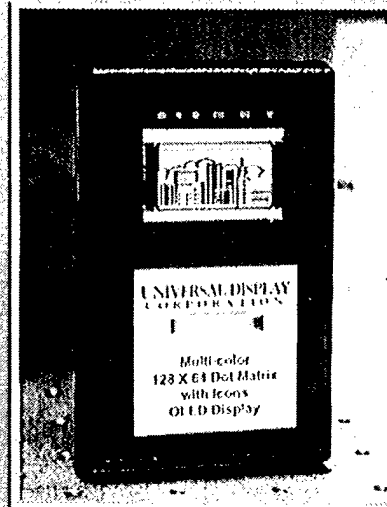
Early SOLED Prototype



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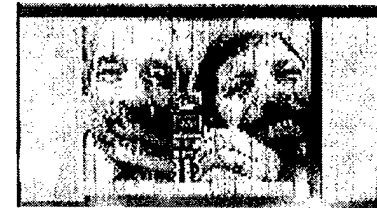
103

First Passive Matrix Prototype



High efficiency materials

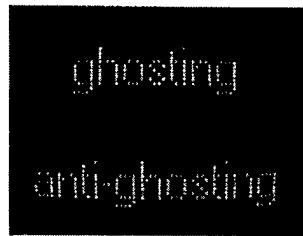
Second Passive Matrix Prototype: PM2



- 128 columns x 64 rows, 80 dpi, 32-level gray scale
- peak current = 0.2 mA (1/64 duty cycle)
- driving voltage = 15V
- pixel active area = H 0.2275 mm x W 0.2475 mm = 0.0563 mm²
- pixel spacing = 0.3175 mm x 0.3175 mm
- fill factor = 56%
- average pixel luminance = 660 cd/m²
at average pixel current density = 5.6 mA/cm²
- nonuniformity <10% (based on VESA FPD std)

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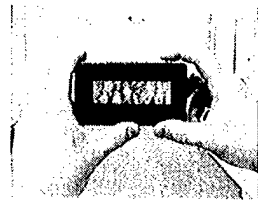
Redesign of PM Drive Scheme: Eliminate Ghosting



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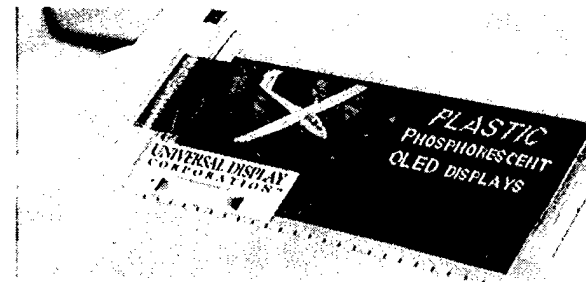
Digital Camera prototype with OLED display: PM4



- Configured to be digital camera or compact video monitor with freeze frame
- 240 columns x 64 rows, 80 dpi, 64-level pulse width modulation gray scale using off the shelf driver chips
- Peak pixel current = 0.18 mA (1/64 duty cycle)
- Driving voltage = 16V typical, maximum system voltage 18V
- Average pixel luminance = 150 cd/m² with circular polarizer
- at average pixel current density = 2.9 mA/cm²
- Four hours with fully charged batteries
- Compact size – 4.5" x 2.5" x 1.25"

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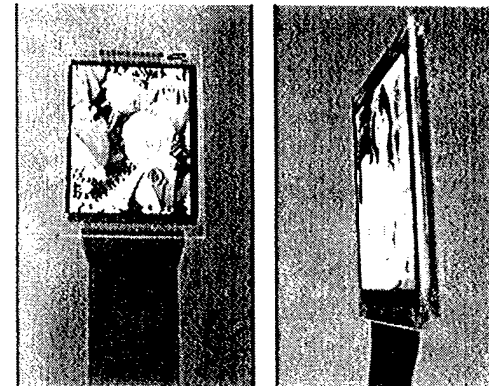
Third Passive Matrix Prototype: PM3



- 256 columns x 64 rows, 80 dpi, 256-level gray scale
- peak current = 0.19 mA (1/64 duty cycle)
- driving voltage = 16V typical,
- pixel active area = H 0.2275 mm x W 0.2275 mm = 0.0518 mm²
- pixel spacing = 0.3175 mm x 0.3175 mm
- fill factor = 51%
- average pixel luminance = 300 cd/m² (without circular polarizer)
- at average pixel current density = 2.9 mA/cm²
- nonuniformity <10% (based on VESA FPD std)

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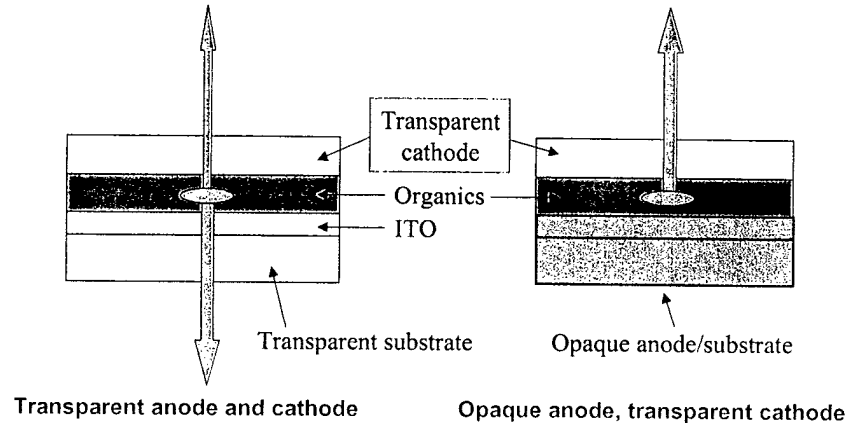
Samsung SDI 2.2" Full-color Display UDC R/G PHOLEDs



ITEMS	SPEC.
Diagonal size (in.)	2.2
Pixel Format	176 (H) x RGB x 220 (V)
Pixel pitch (µm)	66 x 198
Pixel density (in. ⁻¹)	128
Panel size (mm ²)	41.976 (H) x 56.232(V)
Aperture ratio	32%
Luminance (w/o polarizer)(cd/m ²)	200 Peak : >300
White Quality	(0.31,0.32)

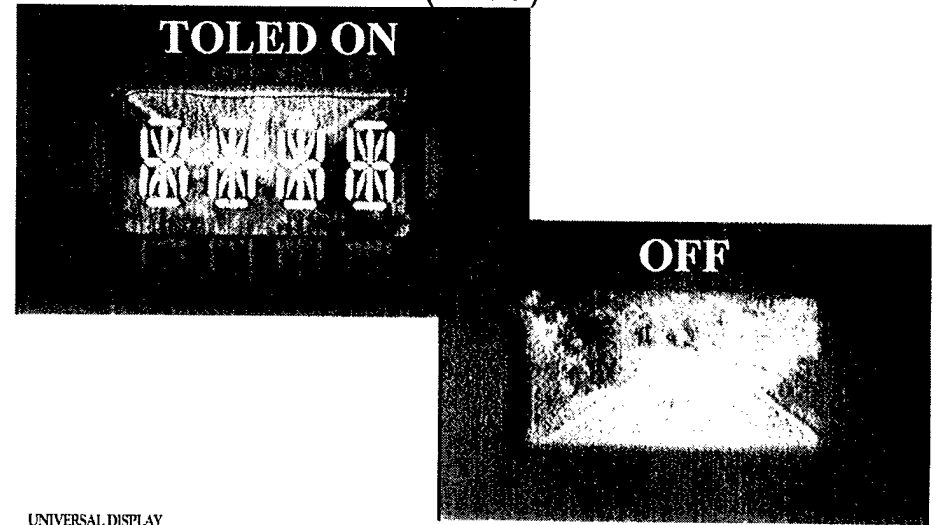
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Transparent vs. Top Emission OLEDs



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Transparent OLED (TOLED) 1st Prototype (1999)



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Transparent OLEDs

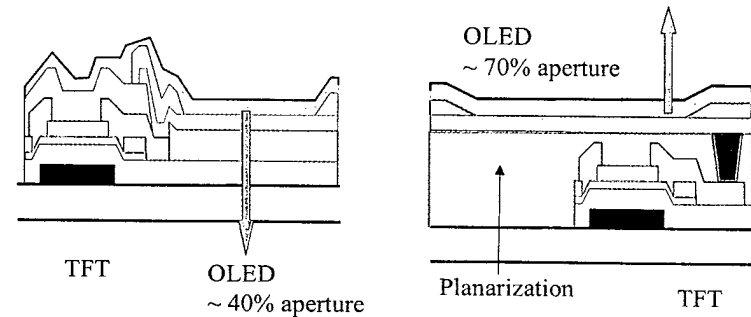
Future vision-area applications

- Top emission for active matrix displays
- Stacked RGB Emitters (tunable color)

Funding from DARPA via AFRL, and US Army (CECOM - NVESD)

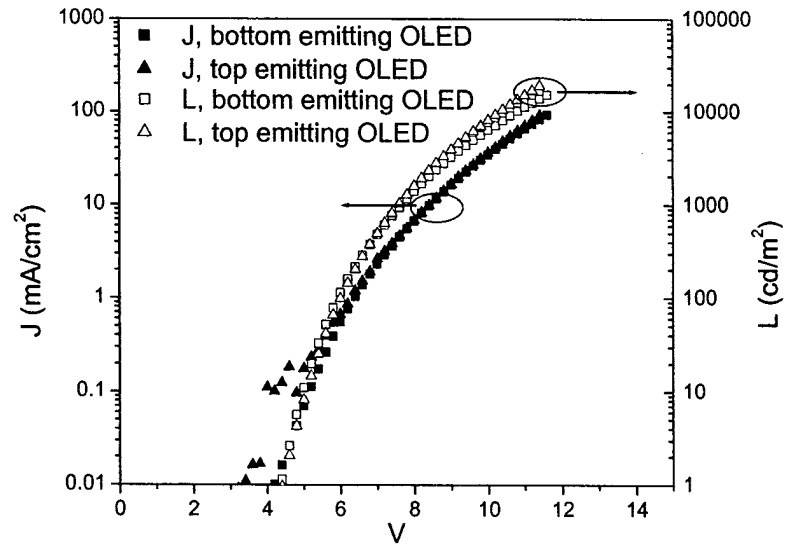
Technical Merits of Top Emission OLEDs

- Potentially higher efficiency than bottom emission device. We have demonstrated TOLEDs as efficient as the bottom emission device on a reflective anode.
- Allows a higher aperture ratio in AMOLED pixels.



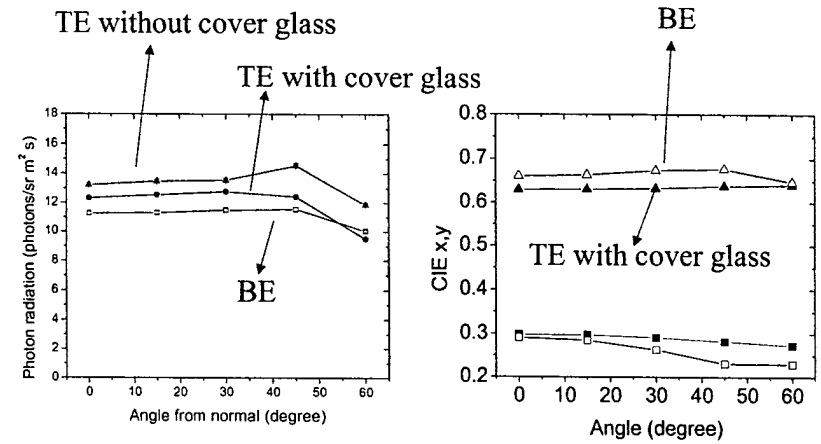
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Green Top Emission Devices



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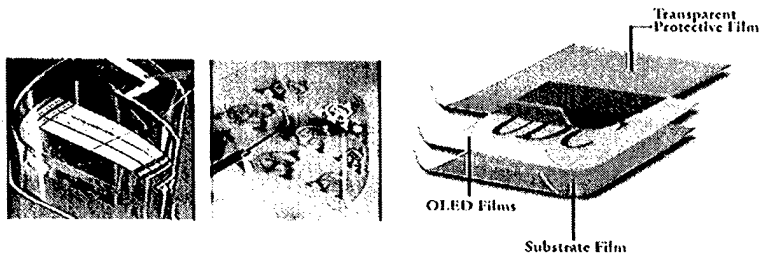
TOLEDs with and without a Cover Glass



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Flexible OLEDs (FOLEDs)



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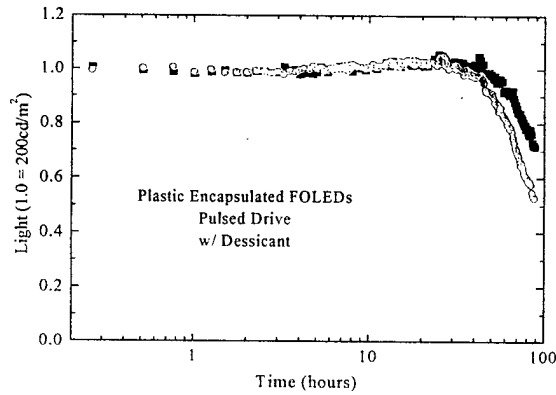
Key FOLED Issues

- Packaging
 - Permeability/OLED lifetime
 - Conformability, flexibility
 - Press durability
- Yield
 - Substrate processibility
 - Temperature and chemical resistance, surface roughness
 - ITO performance and patternability
- Display Fabrication
 - Passive/active matrix architecture
 - Module assembly

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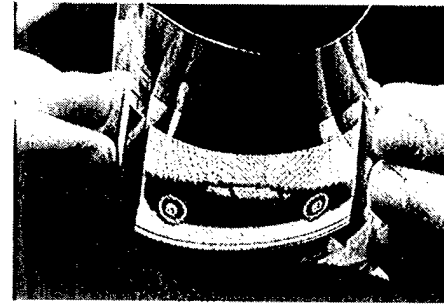
Plastic Encapsulated FOLED

Plastic with No Barrier Coating



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Flexible Display Prototypes



Passive Matrix Built on ITO/Plastic

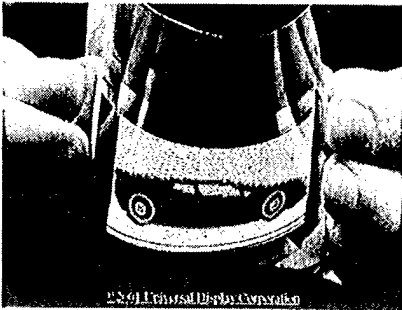


Passive Matrix Built on Battelle
Barrier Coated Plastic

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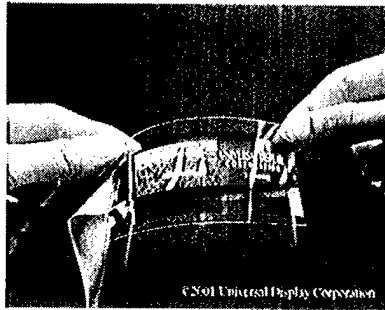
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Flexible Display Progress



2000

- 64 x 128 passive matrix display
- 60 dpi resolution
- 60 Hz refresh rate
- 0.175 mm PET substrate



2001

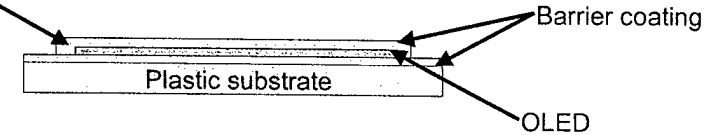
- 64 x 240 passive matrix display
- 80 dpi resolution
- 120 Hz refresh rate
- 0.175 mm PET substrate
- full motion video

U.S. Patent No. 5,844,363

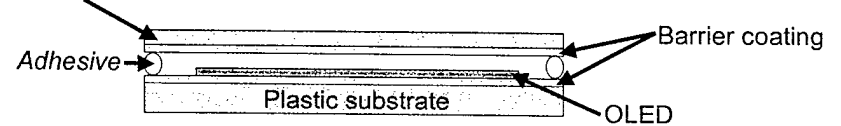
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Flexible Packaging Options

Conformal encapsulation

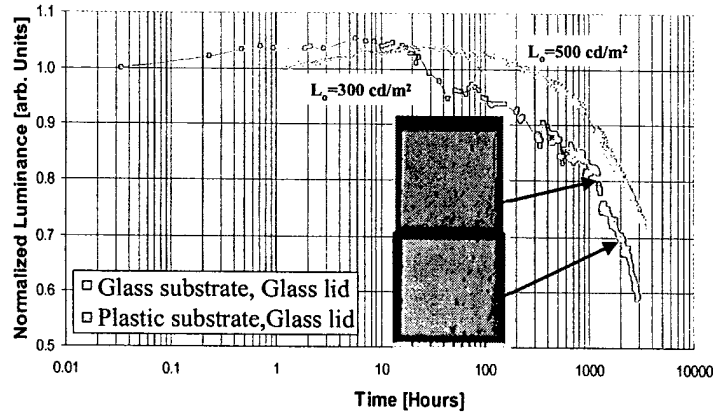


Plastic lid



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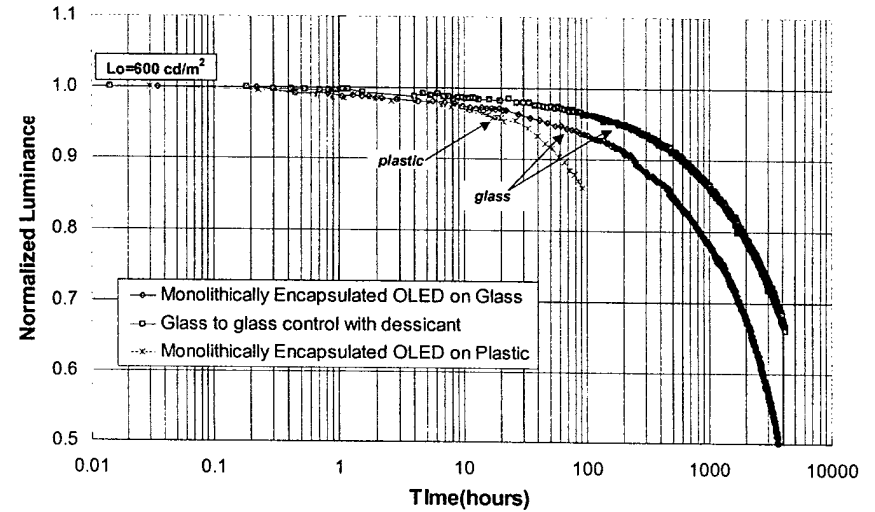
Lifetime of OLEDs on Plastic vs. Glass



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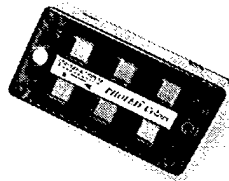
Evaluation of Monolithic Encapsulation



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Phosphorescent OLED Performance

EL color	Deep red	Red	Blue	Green
Peak wavelength (nm)	650	620	474	514
CIE - x	0.71	0.65	0.16	0.30
CIE - y	0.29	0.35	0.37	0.63
Luminance eff @ 1 mA/cm ² (cd/A)	1.0	11	13	24
Lifetime (hours)	100,000 @ 70 cd/m ²	>7,000 @ 300 cd/m ²	under development	>8,000 @ 500 cd/m ²



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Other Key Accomplishments Since 1997

- Transparent/Top Emission TOLEDs
 - Efficiency as high as Bottom Emission
 - Lifetime > 3,000 hours
- Flexible OLEDs
 - Process Yield Understood
 - Demonstrated World's First FOLED Display
 - On our way to enhancing lifetime

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What directions are we headed?

- in the areas from the HDS legacy -

- Reliability
 - Developing Epoxyless Packages
 - Developing New Materials and Improved Architectures
 - Maximizing the Efficiency x Lifetime Product
 - Investigating High Temperature Operation
- Prototypes
 - Flexible Displays
 - AMOLED Prototypes with Partners
 - Transparent Displays
- Pilot Line.... I.e. building the business

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The Business

TECHNOLOGY DEVELOPMENT

- *Cutting-edge research & development*
- *Expanding intellectual property portfolio*
- *Process development & product prototyping*



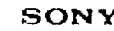
TECHNOLOGY TRANSFER

- *Patents, know-how and training*
- *High-purity organic materials*
- *Next-generation OLED deposition equipment*



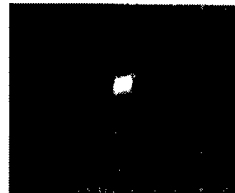
COMMERCIALIZATION PARTNERSHIPS

- *Co-development programs*
- *Licensing*
- *Joint ventures*



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First OLED on OVPD Pilot Line System



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Thanks for your support!

Thanks to the Entire Teams of UDC,
Princeton University and University
of Southern California for an
Awesome Collaboration

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