Materials and Architectural Development in White OLEDs

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New Industrial Chemistry and Engineering Workshop
OLED Materials for Lighting and Display
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Outline:

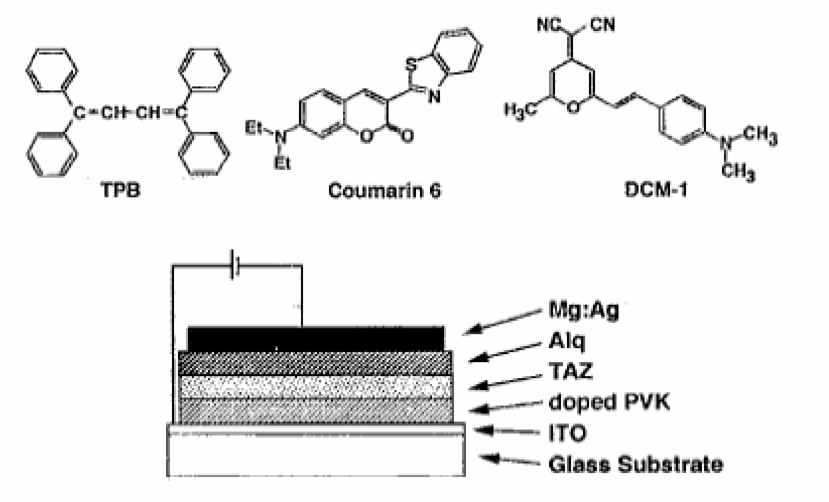
- ☐ Introduction to white OLED technology
- ☐ Architectures and materials for phosphorescent OLEDs (PHOLEDs): hosts, architectures, performance challenges
- ☐ High efficiency, multi-stacked hybrid white OLEDs
- ☐ Single-stack hybrid white OLEDs:
  - ✓ Harvesting white OLEDs– a route to efficient white devices

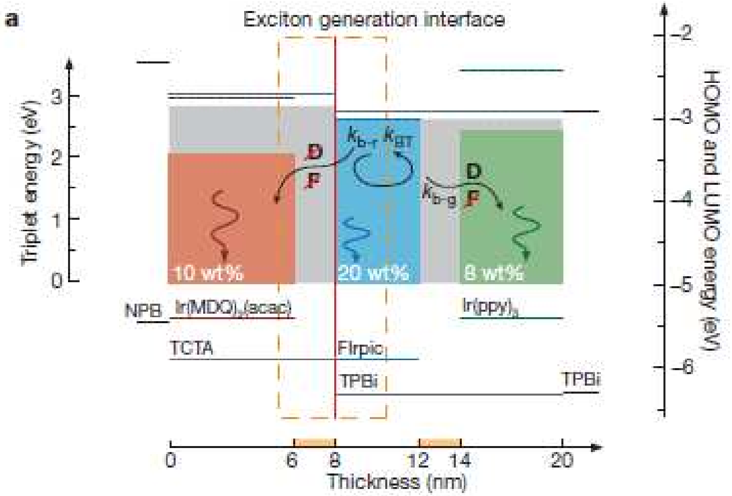
White OLED technology

White OLED is critical and scalable technology for enabling energy-efficient displays and SSL

0.83 lm/W at 50 cd/m^2

90 lm/W at 1000 cd/m^2

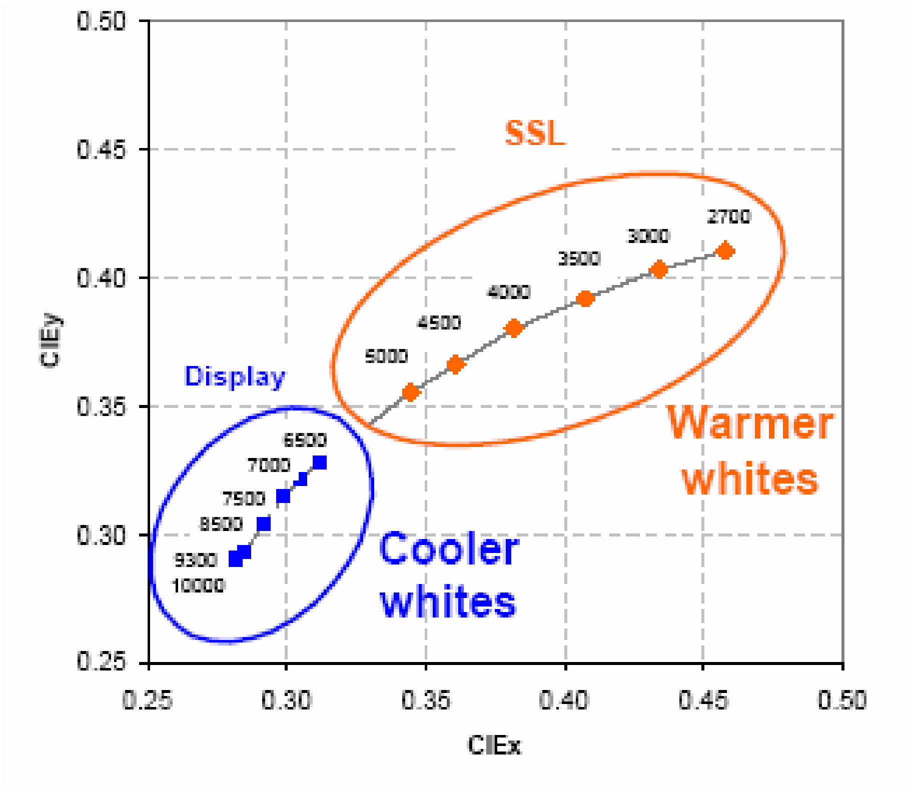




Kido et al, Appl.Phys.Lett., 1994

Reineke et al, Nature, 2009

Synergy between WOLED for displays and SSL



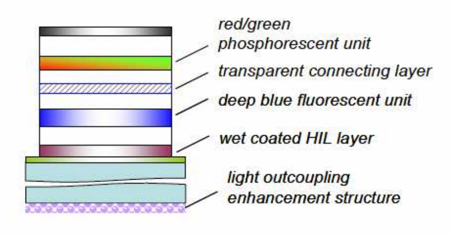
Source: Hatwar et al., SID'10

Color temperature is adjusted by manipulation of the architecture and material formulation

Kodak SID 2009

Various approaches to WOLED development

- ☐ 1-stack or tandem structures
- ☐ Vacuum deposited (VTE) or solution processed
  hybrid approach is possible
- ☐ RGB (FMM), white with CF, printing, etc

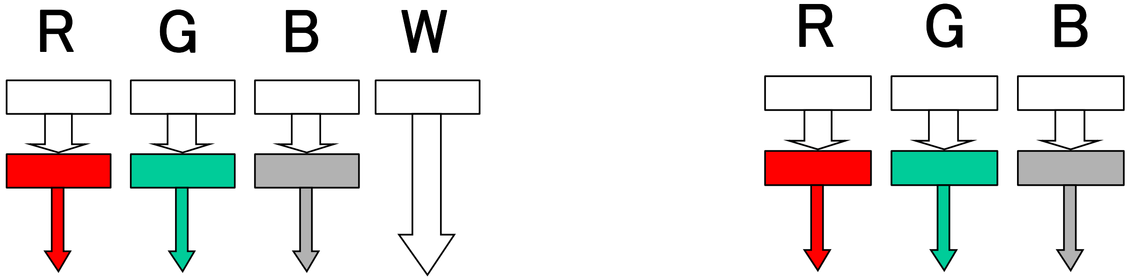


Source: Komoda, SID'10 and SID'11

Each architecture has its advantages and performance trade-off

OLED for display – white with color filters

- High production technology:
  - No mask-related defects
  - Glass size: > Gen 6
  - In line process
- RGBW 4-pixel architectures – lower power consumption
- 3D friendly



Source: LG Display, SID'10
Young, Inf.Display, 26(10), 2010

OLED lighting:

- Large-area diffuse light source:
  - ✓ Less glare
  - ✓ Less fixture loss
  - ✓ High luminaire efficacy, lower power usage
- Thin, flat, lightweight
- Fast switch-on; fully dimmable
- Wide range of colors possible
- "Green" technology – no mercury
- Possibility for features:
  - ✓ Flexible
  - ✓ Transparent
  - ✓ Color tunable

Source: OLED-Info

Source: Levemore, Inf.Display, 26(10), 2010

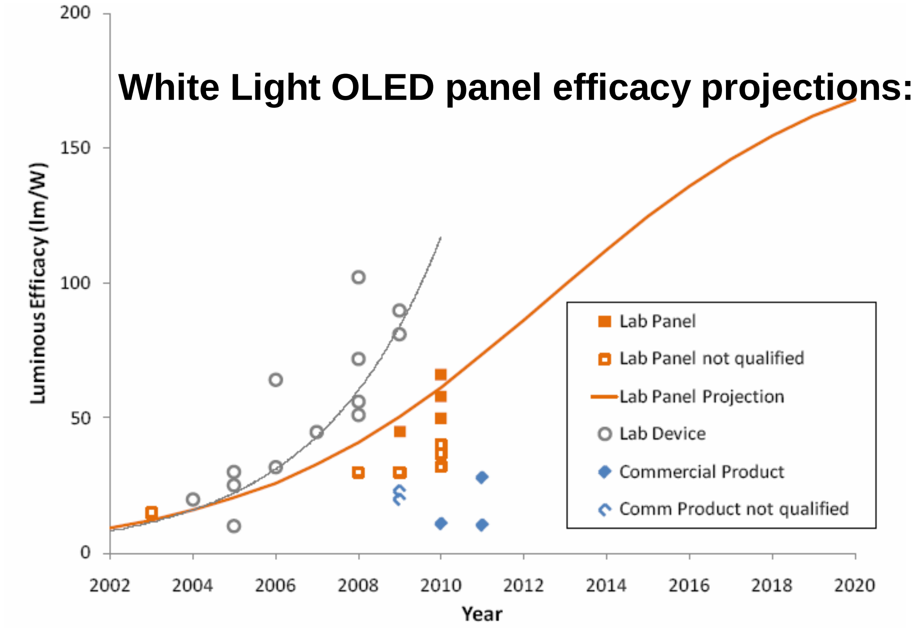
Efficiency requirements for OLED panels

DOE projections are based on results obtained with panels

Metric	2010	2012	2015	2020
Panel efficacy, lm/W	62	86	125	168
LT$_{70}$, Khours	10	25	50	100
Lum. emittance, lm/m^2	3.000	6.000	10.000	10.000

CRI>85, 2580-3710 K
Panel size of at least 200 cm^2

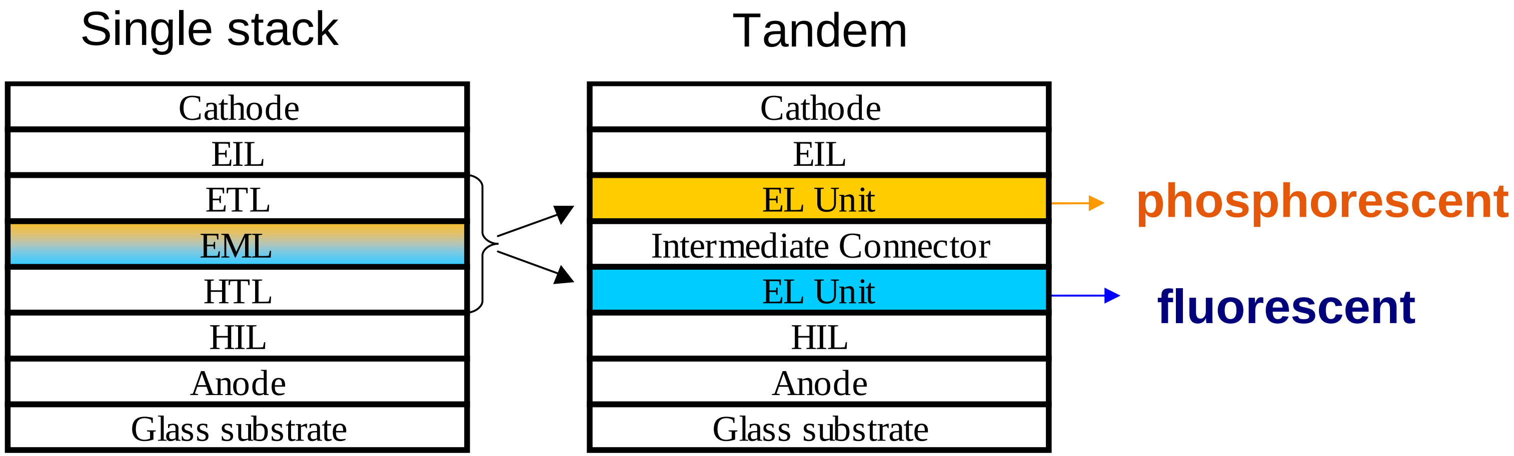
Source:MYPP, updated May 2011, table 5.8
http://apps1.eere.energy.gov/buildings/publications/pdfs/ssl/ssl_mypp2011_web.pdf


White Light OLED panel efficacy projections:

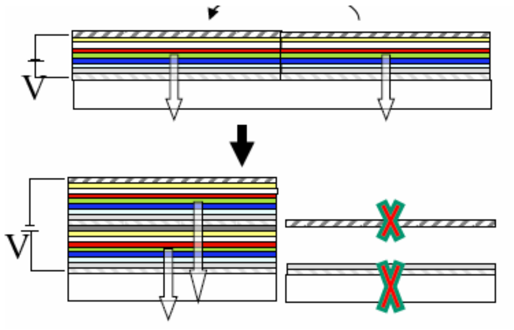
Efficiency targets cannot be met without use of phosphorescent OLED technology

Hybrid White OLED architecture

Hybrid *≡ Both fluorescent and phosphorescent emitters in same OLED*



- Significant LT improvement
- Efficacy improvement
- Flexibility in color adjustment
- Ease in construction of hybrid OLEDs
- Reduced IR loss



Twice the OLED in the same area

Source: Tyan, DOE Workshop 2010

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  - ✓ Harvesting white OLEDs– a route to efficient white devices

Phosphorescent host requirements

1. Triplet energy (E_T)

Color	HOMO-LUMO, eV	E_S, eV	E_T, eV
Red	2.8	2.7	2.1
Green	3.4	3.2	2.5
Blue	3.7	3.4	2.7

✓ Energy transfer from both the host singlet and triplet excited states to the dopant triplet excited state

✓ Direct trapping of charge on the dopant (more efficient devices)

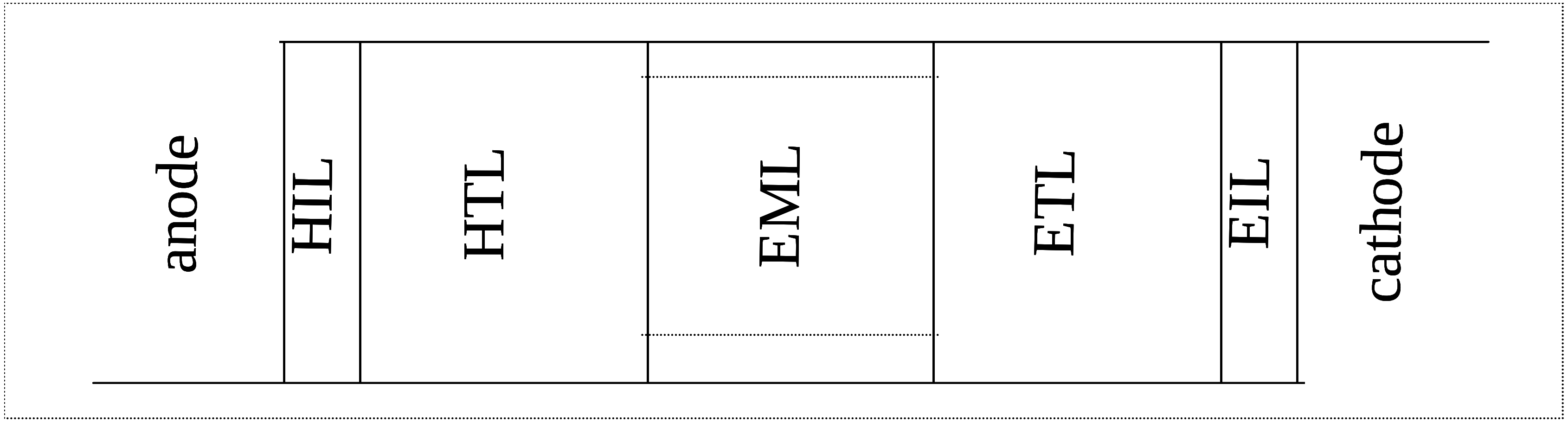
2. Charge transporting properties

3. HOMO(IP)/LUMO(EA) alignment of host(s) with ETL & HTL

4. Chemical and thermal (T_s<500ºC, T_m>100ºC) stability

Difficult to meet criteria with the same material!

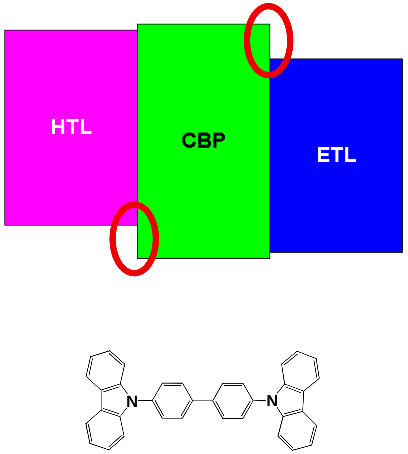
“Ideal” OLED device – Low Voltage, High Efficiency

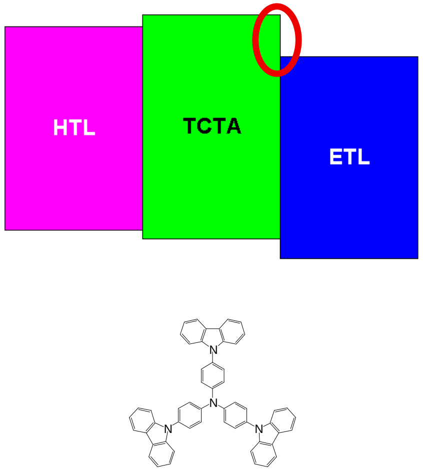


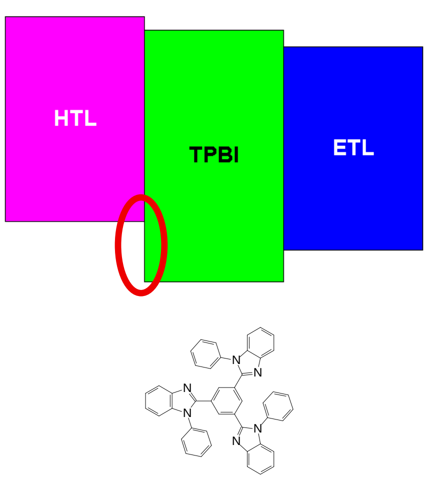
- Barrier-less injection/transport of electrons and holes (V_{bi} > 2.0-2.2V)
- High mobility transport materials
- High mobility host
- Dopant trapping (direct excitation)
- No unnecessarily large bandgaps (including transport materials)

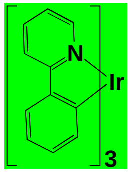
Architecture – Host type

1. Single (Bipolar, Unipolar) Host





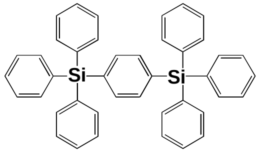




Ir(ppy)$_3$

Large barrier to charge injection at HTL and/or ETL interface
Recombination at interfaces

2. Inert matrix host



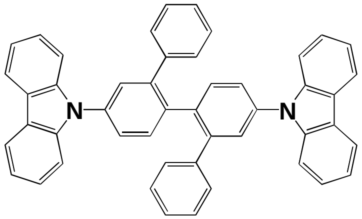
UGH2

UGH type, phosphorescent dopant carries charges
Usually high-voltage devices

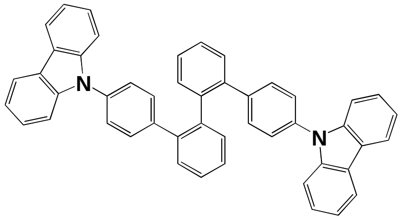
3. Mixed host

Single host : high energy materials

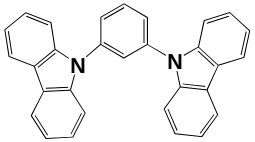
High energy carbazoles (hosts):



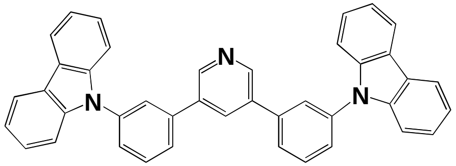
CBDP
2.8 eV



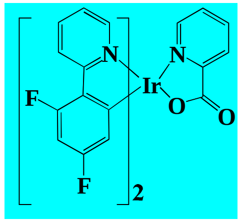
BCBP(1)
2.7 eV



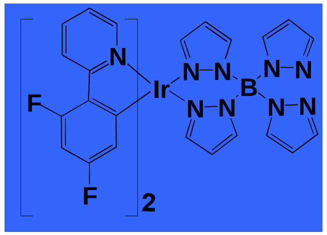
mCP
2.9 eV



26DCzPPY(2),
2.7 eV
23% EQE, 35 lm/W

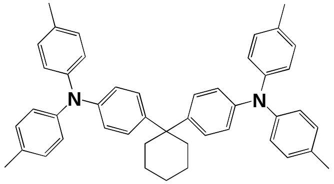


FIrpic

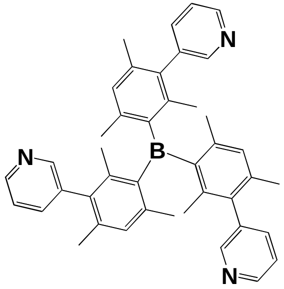


FIr6

Charge transport:



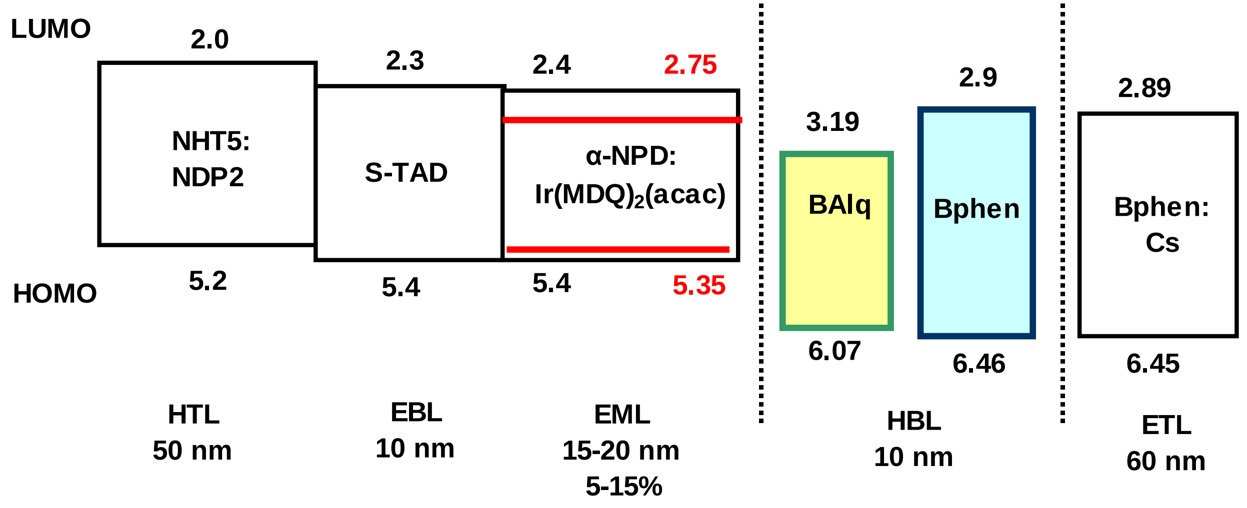
TAPC(4)
2.95 eV
$\mu \sim 7 \times 10^{-3}$ cm^2/Vs



3TPYMB(3)
2.98 eV
$\mu \sim 10^{-5}$ cm^2/Vs

1. *L. Xiao et al., Adv.Mat., 21, 1271, 2009*
2. *S. Su et al., Chem.Mater.,28,1691, 2008*
3. *D. Tanaka et al., Jpn.J.Appl.Phys, 46, L117, 2007*
4. *N.Chopra et al., Appl.Phys.Lett., 93, 143307, 2008*

Single unipolar host



LUMO

HOMO

2.0

NHT5:
NDP2

5.2

HTL
50 nm

2.3

S-TAD

5.4

EBL
10 nm

2.4 2.75

α-NPD:
Ir(MDQ)$_2$(acac)

5.4 5.35

EML
15-20 nm
5-15%

3.19

BAlq

6.07

2.9

Bphen

6.46

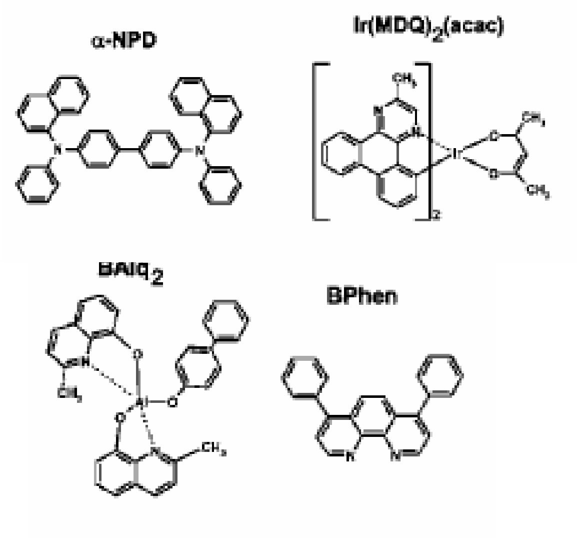
HBL
10 nm

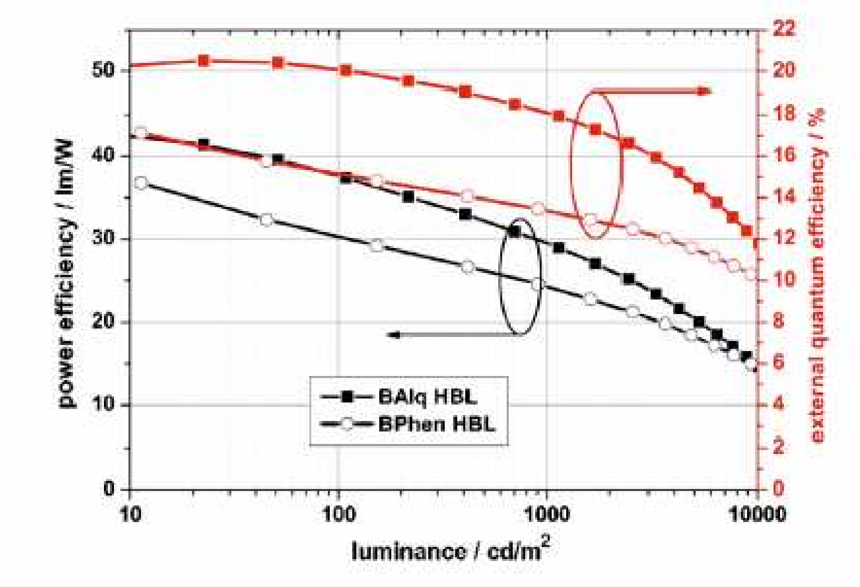
2.89

Bphen:
Cs

6.45

ETL
60 nm





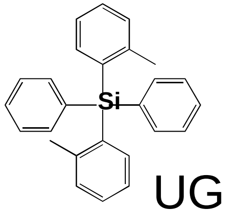
Dopant (10%) transports electrons
610 nm, (0.63, 0.37)

At 100 cd/m^2 :
20%EQE, 32 cd/A with BAlq

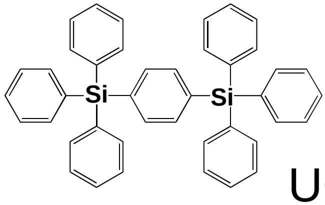
LT$_{50}$=600 h at 6000 nits (5% dopant)
LT$_{50}$=1600 h at 6000 nits (15% dopant)

R. Meerheim et al, J.Appl.Phys., 104, 014510, 2008

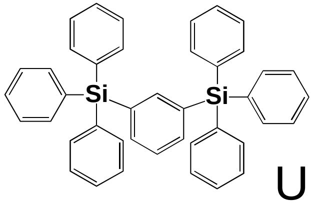
Host type – Inert matrix



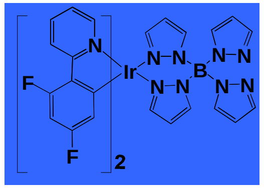
UGH1



UGH2

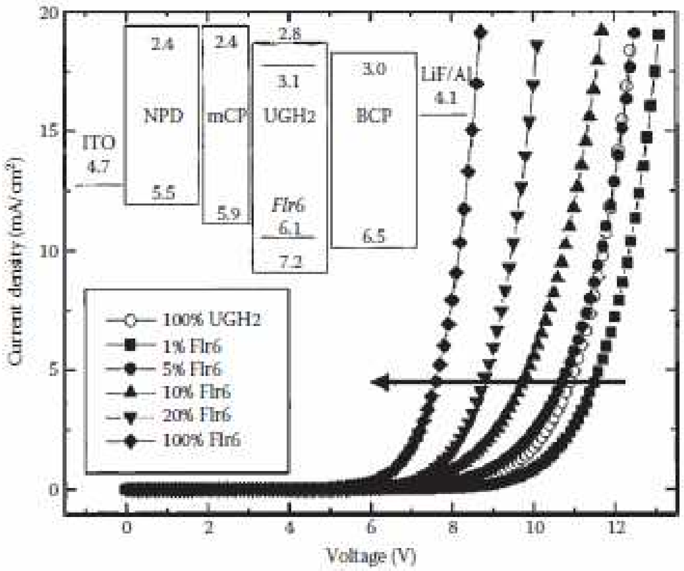


UGH3



Triplet energy : 3.5 eV
HOMO : –7.2 eV
LUMO : –2.8 eV

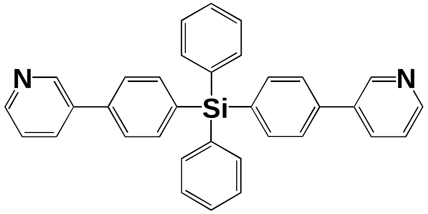
X.Ren et al., Chem.Mater., 2004



R.Holmes et al, Appl.Phys.Lett.,83, 3818,2003

FIr6 transports charges in the EML
Host is not electrically excited

11.6% EQE, 13.9 lm/W, (0.16, 0.26)



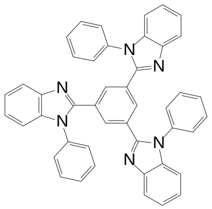
Triplet energy : 2.7eV
IP : 6.5 eV
EA : 2.5 eV

Xiao et al, Adv.Mater., 21, 1271, 2009

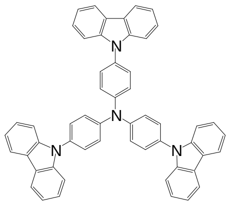
Mixed host :

- Consists of hole (h^+)- and electron (e^-)-transporting components;
- Because e^- and h^+ are carried by different materials, HOMO/LUMO levels can be adjusted independent of triplet energy;
- Improves charge injection and transport;
- Eliminates/reduces internal charge accumulations at/near interfaces;
- Results in improved device performance.

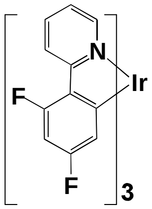
Model mixed host materials for green and blue PHOLEDs: TPBI+TCTA



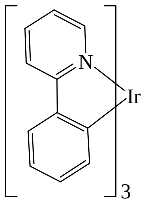
TPBI
E_T=2.74 eV



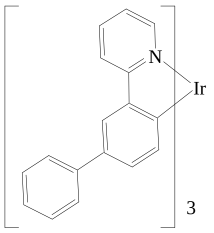
TCTA
E_T=2.85 eV



$Ir(F_2ppy)_3$
E_T=2.71 eV



$Ir(ppy)_3$
E_T=2.54 eV

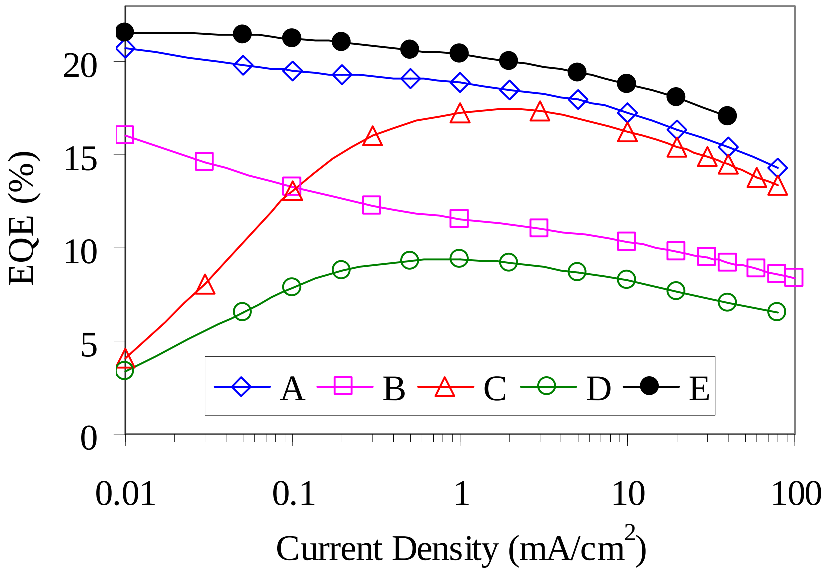


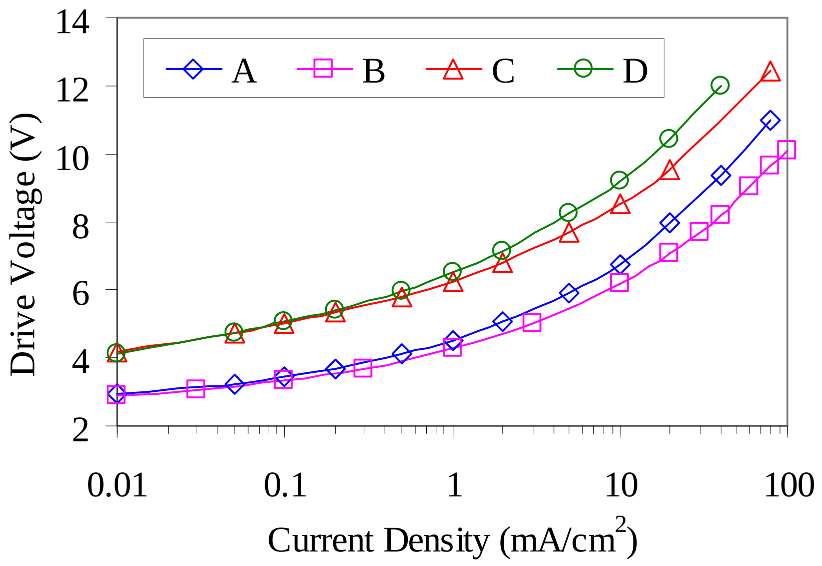
$Ir(5'\text{-ph-ppy})_3$
E_T=2.59 eV

Kondakova et al, SID'07
Kondakova et al, J.App.Phys., 104, 094501, 2008

Mixed TPBI+TCTA vs neat CBP host

Voltage reduced by ~2V, Power efficiency increased by 30%





Organic layers:

(A) NPB (95 nm) | TCTA (10 nm) | TPBI+TCTA+ 6% Ir(ppy)$_3$ (35nm)
(B) NPB (105 nm) | TPBI+TCTA+ 6% Ir(ppy)$_3$ (35 nm)
(C) NPB (95nm) | TCTA (10 nm) | CBP+6% Ir(ppy)$_3$ (35 nm)
(D) NPB (105nm) | CBP+6% Ir(ppy)$_3$ (35 nm)

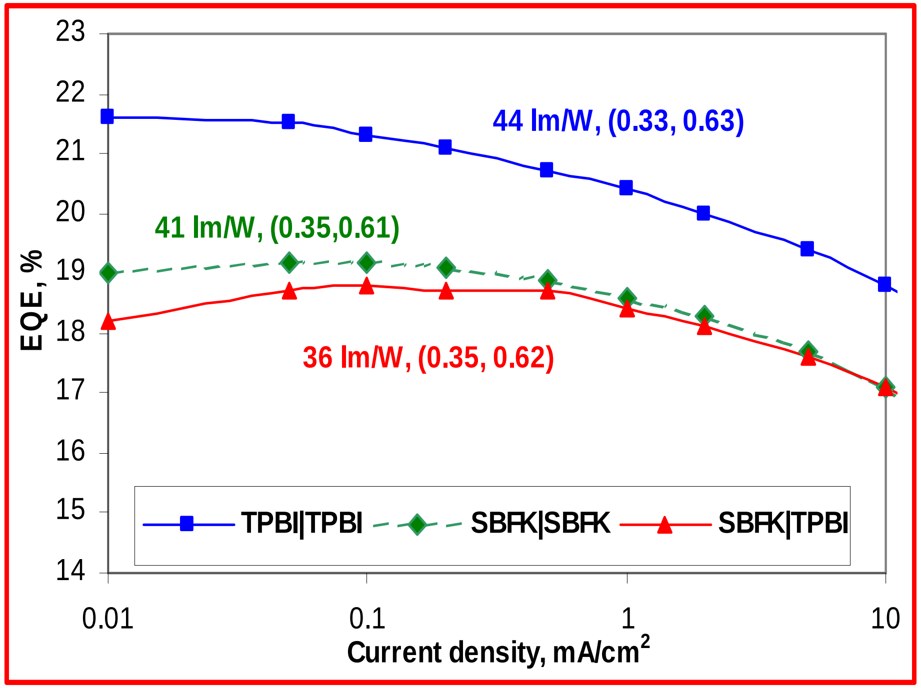
BALQ' (10 nm)|ALQ (40 nm) were used as HBL|ETL

(E): NPB (85nm) | TCTA (10nm) | TPBI+TCTA+ 10% Ir(5'-ph-ppy)$_3$ (35nm) | TPBI (10nm) | Alq (40nm)

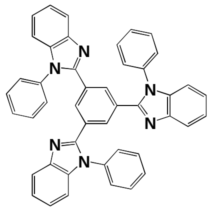
Kondakova et al, J.App.Phys., 104, 094501, 2008

Replacing TPBI with stable ET co-host

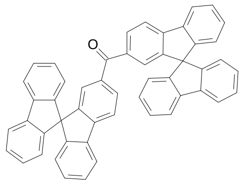
NPB | TCTA | ET co-host + 30%TCTA + 10%Ir(5'-ph-ppy)$_3$ | HBL | Alq | LiF | Al



Inset data @1000 nits

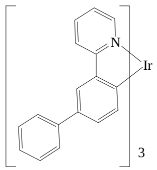


TPBI



SBFK

E_T=2.62 eV

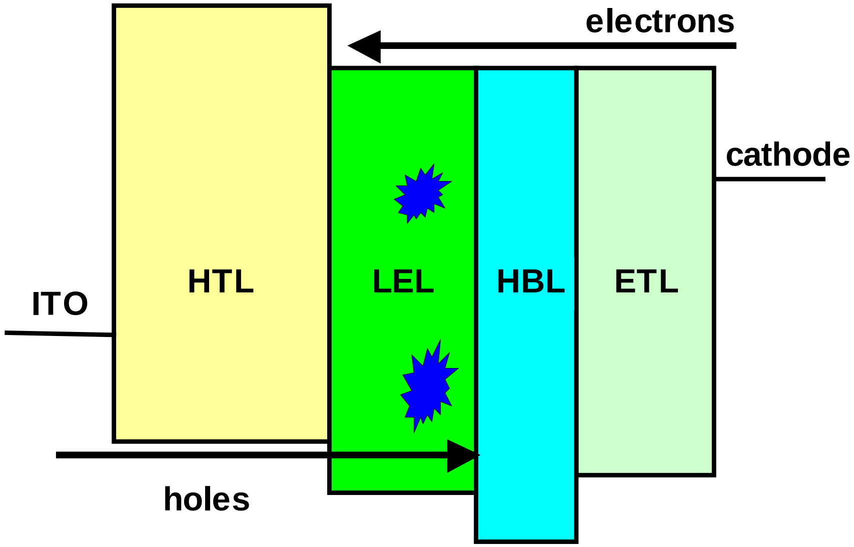


Ir(5′-ph-ppy)$_3$

Co-host	HBL	T50 @1000 nits
TPBI	TPBI	500
SBFK	TPBI	5300
SBFK	SBFK	6500

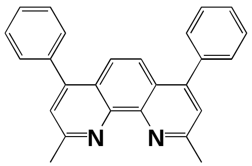
Kondakova et al, J.App.Phys., 104, 094501, 2008

Hole/exciton blocking materials (HBM)



High energy electron transport materials

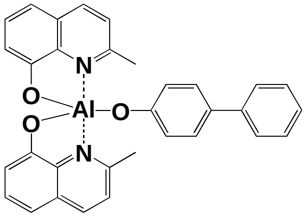
E_T HBM > E_T emitter



BCP

E_T= 2.5 eV

t_{50} <700 h

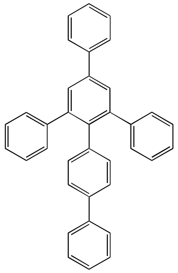


BAlq

E_T= 2.3 eV

t_{50} <10,000 h

R. Kwong, Appl.Phys.Lett., 81,162, 2002



E_T=2.5 eV

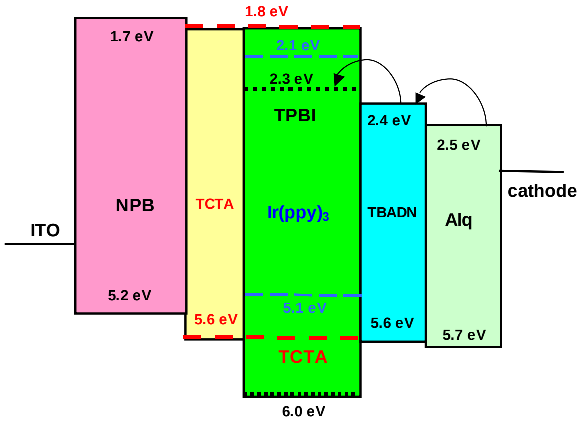
HOMO= -6.2 eV

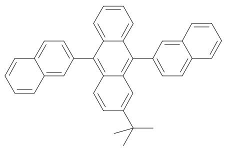
LUMO= -2.6 eV

V.Adamovich, Org. Electron., ***4*** *(2003), 77.*

Mixed-host PHOLED does not require HBM

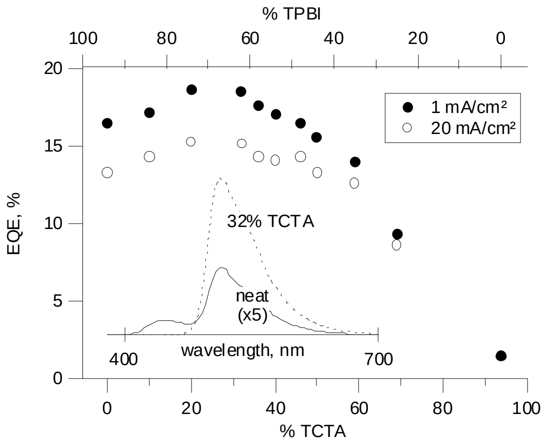
- Transport properties of EML in mixed-host devices can be easily adjusted
- Triplet energy of HBM is/can be made irrelevant
- HBL selection is based on electron injection (LUMO) and transport properties

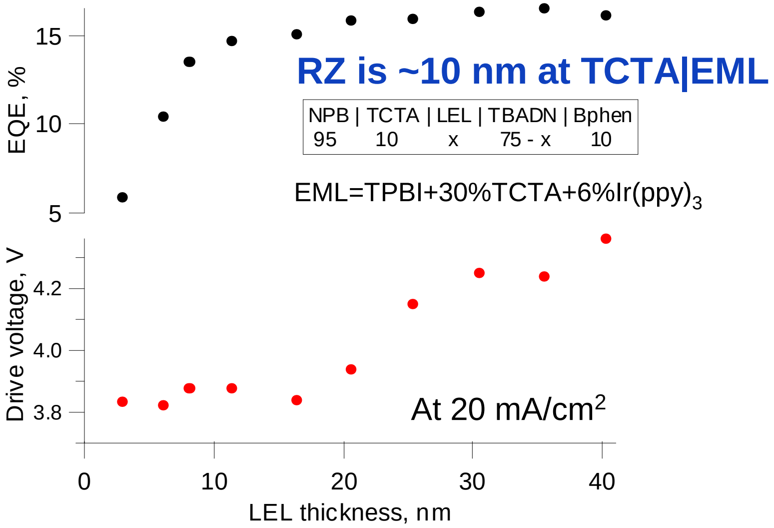




TBADN, E_T=1.84 eV

Ir(ppy)$_3$, E_T=2.49 eV





RZ is ~10 nm at TCTA|EML

NPB	TCTA	LEL	TBADN	Bphen
95	10	x	75 - x	10

EML=TPBI+30%TCTA+6%Ir(ppy)$_3$

At 20 mA/cm^2

Kondakova et al, SID'07
Kondakova et al, J.App.Phys., 104, 094501, 2008

Voltage reduction in green PHOLEDs: no HBL architecture

NPB | TCTA | TPBI+TCTA+Ir(ppy)$_3$ | ETL | EIL | LiF | Al

@1000 nits

ETL|EIL	Volts	lm/W	EQE, %	
Alq	5.0	35.6	16.2	
TPBI | Alq	5.5	40.3	18.9	Better confinement of triplet exitons
TBADN | Alq	4.1	48.4	18.8	Lower e$^-$ injection barrier
TBADN | Bphen	3.2	64.0	19.1	Lower e$^-$ injection barrier, better e$^-$ transport

2.3 V reduction at ~ 2 mA/cm^2
~3V at 20 mA/cm^2

Similar voltage reduction for blue PHOLEDs

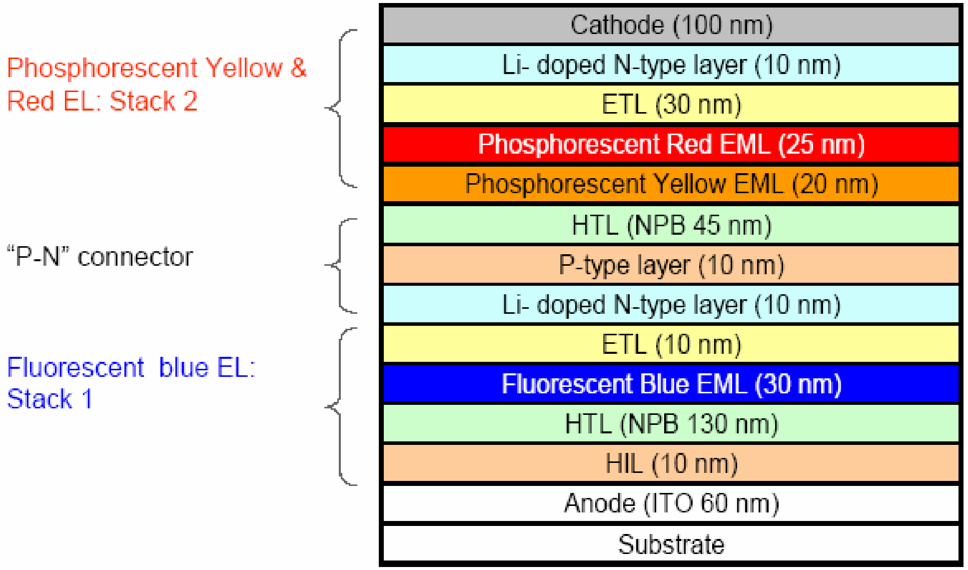
Kondakova et al, SID'07
Kondakova et al, J.App.Phys., 104, 094501, 2008

Outline:

- ☐ Introduction to white OLED technology
- ☐ Architectures and materials for phosphorescent OLEDs (PHOLEDs): hosts, architectures, performance challenges
- ☐ High efficiency, multi-stacked hybrid white OLEDs
- ☐ Single-stack hybrid white OLEDs:
  - ✓ Harvesting white OLEDs– a route to efficient white devices

Performance of hybrid tandem WOLED for SSL

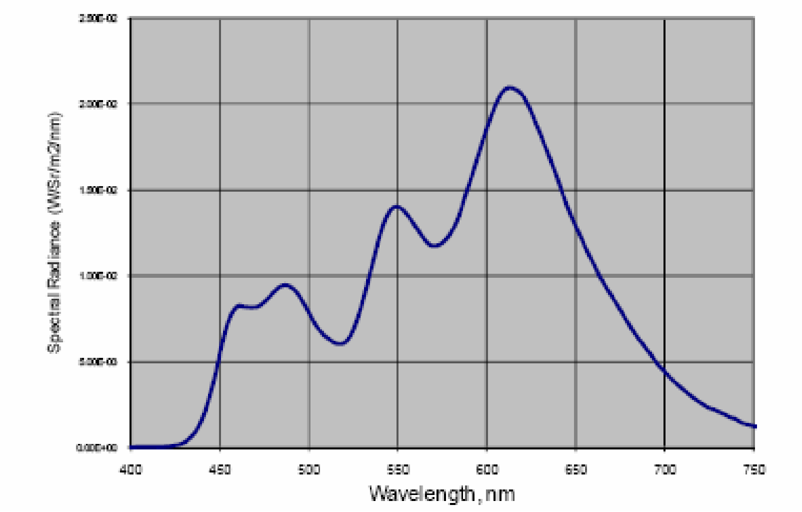
Device type	V	cd/A	EQE%	CIEx	CIEy	lm/W	Half life, T50 @1000 cd/m2 (h)
Device 12: (EK9 blue dopant in stack 1 and EK532 yellow dopant in stack 2)	6.5	48.7	28.4	0.43	0.32	23.6	125,000
Device 13: (New blue dopant in stack 1 and EK532 yellow dopant in stack 2)	6.5	51.3	30.6	0.40	0.30	24.7	72,000

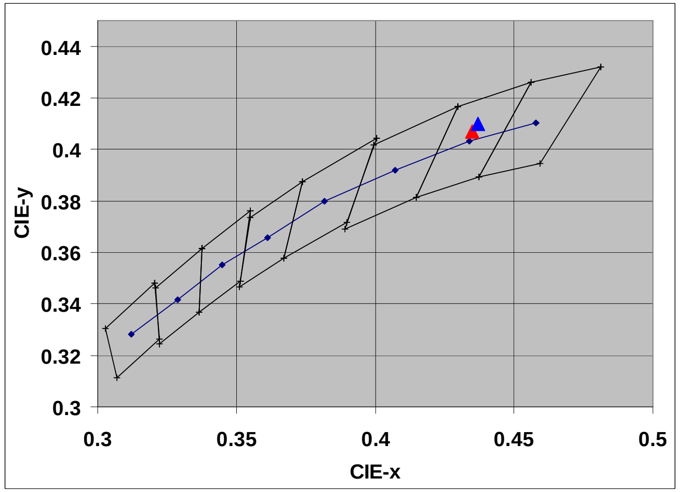


No outcoupling enhancement

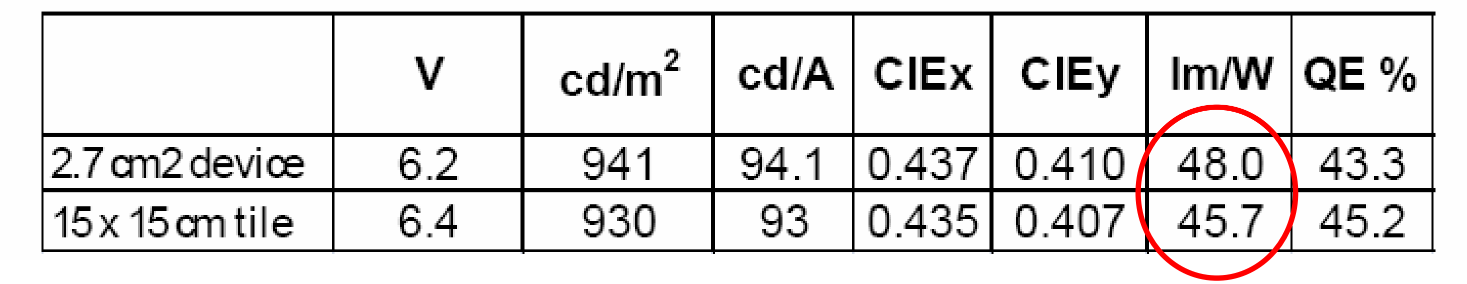
This work was carried out at Eastman Kodak Company prior 12/ 2009
Hatwar et al., SID'10

Performance of 15 x 15 cm OLED SSL lighting panel using hybrid tandem





Performance of a 15 cm × 15 cm OLED lighting panel and a 2.7 cm^2 OLED device



	V	cd/m^2	cd/A	CIEx	CIEy	lm/W	QE %
2.7 cm2 device	6.2	941	94.1	0.437	0.410	48.0	43.3
15 x 15 cm tile	6.4	930	93	0.435	0.407	45.7	45.2

With external extraction layer

This work was carried out at Eastman Kodak Company prior 12/ 2009
Hatwar et al., SID'10

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State-of-the-art white OLEDs

Fluorescent white OLED single stack:

37 lm/W, 16% EQE, (0.47,0.42), LT_{50}= 15Kh, with extraction layer
20.5 lm/W, 8.5% EQE, w/o light extraction

Novaled (Murano, SID'11)

22 lm/W, 10.7% EQE, (0.41,0.44) at 10 mA/cm^2; LT_{50}= 86Kh

IDK (Kawamura,SID'10)

Phosphorescent emission-based white OLED single stack:

72 lm/W, 42% EQE, (0.46,0.42),CRI=86, 2580K, LT_{70}=55 Kh (outcoupling 2.12x)

UDC (Levermore, SID'11)

80 lm/W, (0.43,0.44), CRI=83, LT_{50}=10 Kh with extraction layer

Panasonic (Komoda, SID'11)

Multi-stack hybrid OLED:

66.4 lm/W, (0.39, 0.39), CRI=85, 3691K with internal extraction layer (2.9X)

Kodak (Tyan, SID'09)

56 lm/W, (0.42, 0,41), CRI=91, 3200K, LT_{50}=150 Kh with internal extr. layer

Panasonic (Komoda, SID'11)

63.6 lm/W, (0.46, 0.40), CRI=78, 2568K, LT_{50}=55 Kh with internal extr layer (2.05x)

Philips (Loebl, SID'11)

OLEDWorks

Phosphorescent emitters

PHOLED Performance (at 1000 cd/m^2)	1931 CIE Color Coordinates	Luminous Efficiency (cd/A)	Operating Lifetime (hrs) LT 95%	LT 50%
DEEP RED	(0.69, 0.31)	17	14,000	250,000
RED	(0.66, 0.34)	24	25,000	600,000
RED	(0.64, 0.36)	30	50,000	900,000
GREEN-YELLOW	(0.46, 0.53)	72	70,000	1,400,000
GREEN	(0.34, 0.62)	78	18,000	400,000
LIGHT BLUE	(0.18, 0.42)	47	600	20,000

Source: www.universaldisplay.com
http://www.universaldisplay.com/default.asp?contentID=604

UNIVERSAL DISPLAY CORPORATION

Stable deep blue phosphorescent emitter is challenge

Company	**Year**	**Cd/A**	**EQE, %**	**CIE x,y**	**Max, nm**	**LT_{50}, h**	**LT reported**
UDC	2006 (oled-info 1/12/2006)	21	11	0.16, 0.29		3 K	500 cd/m^2
Konica-Minolta	SID'07	42	17		472	16 K	300 cd/m^2
UDC	SID'11	47	20	0.18, 0.42	474	20 K	1000 cd/m^2
UDC	SID'11	69	31		474		

University of Southern California
Princeton University
Army Research Laboratory

→ Deep-blue phosphorescent emitters, LT not practical

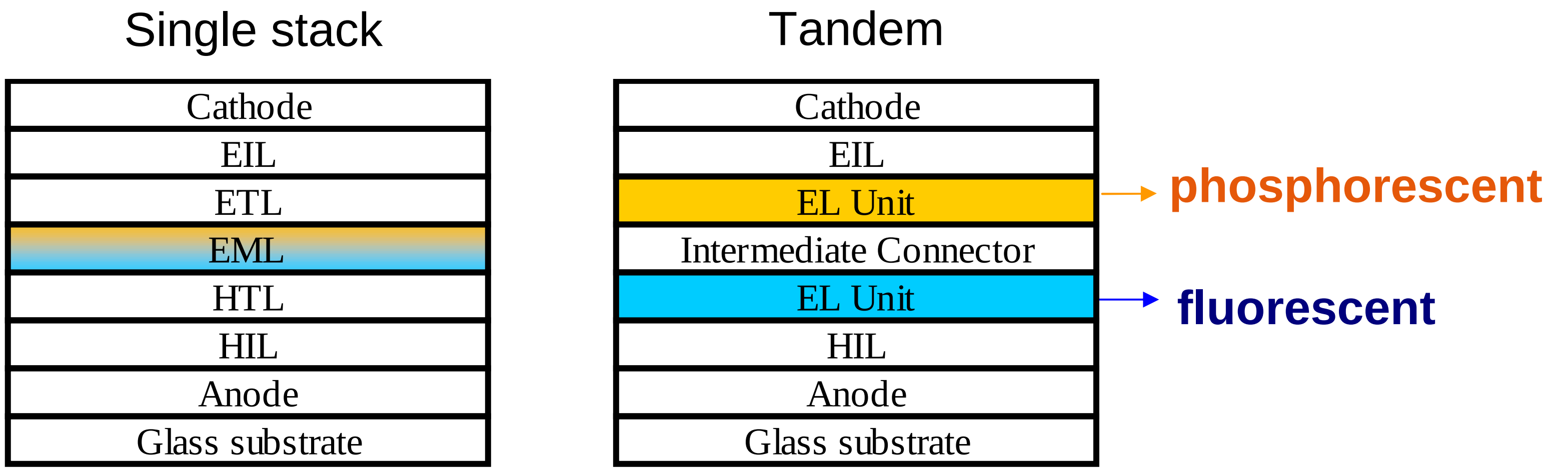
Blue fluorescent emitters status

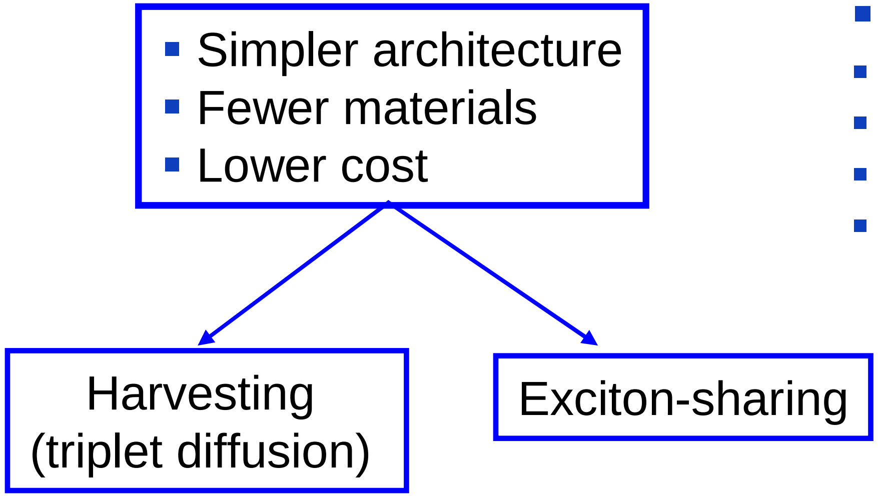
Demonstrated superior lifetime

Emitter / Company	Cd/A	EQE, %	V	LT_{50}, h	CIE x,y	LT_{50} at cd/m^2	Refs
BD-5, **IDK**	8.4			50K	0.13, 0.21	1000	SID’08
EK 9, **Kodak**	8.6	6.3	4.4	10K	0.14, 0.18	1000	SID’08
Dupont	4.7		5.1	39K	0.14, 0.11	1000	SID’10
Dupont	3.2		5.1	9K	0.14, 0.08	1000	SID’10
BD-6, **IDK**	9.0	8.7	4.0	11K	0.14, 0.12	1000	SID’10
BD-6 with EEL1, **IDK**	9.9	9.5	4.0	11K	0.14, 0.12	1000	SID’10
CDT	9.2		4.5	15K	0.14, 0.14	1000	SID’11
BD-7, **IDK**	5.5	7.1	3.9	11K	0.14, 0.08	500	SID’11
BD-7 with EEL2, **IDK**	6.5	8.7	3.8	9K	0.14, 0.078	500	SID’11

Hybrid White OLED architecture

Hybrid *≡ Both fluorescent and phosphorescent emitters in same OLED*





- Simpler architecture
- Fewer materials
- Lower cost

- Significant LT improvement
- Efficacy improvement
- Flexibility in color adjustment
- Ease in construction of hybrid OLEDs
- Reduced IR loss

Single stack hybrid white devices

Hybrid ≡ Both fluorescent and phosphorescent emitters in same OLED

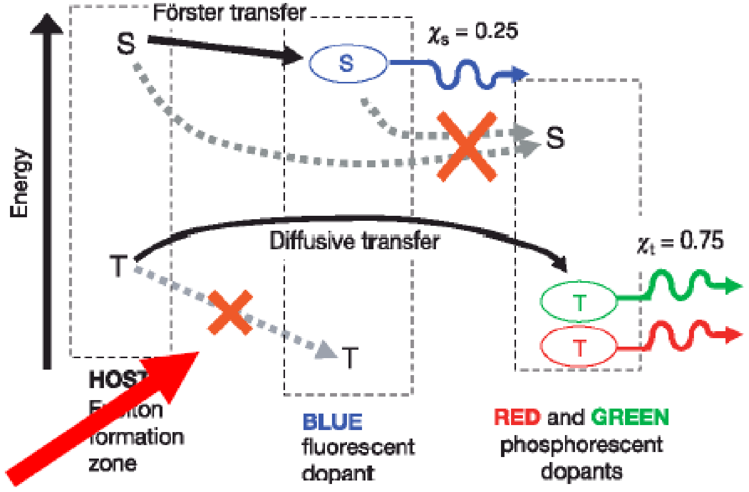
Exciton-sharing hybrid device:

- Phosphorescent green and red
- Fluorescent blue (limited to 25% IQE)
- Recombination takes place in all light emitting layers
- Waste 75% of blue excitons
- Efficiency is high compared to all-fluorescent devices
- Lower voltage compared to multi-stacked OLED

Challenges: color change with time

Single-stack harvesting hybrid white devices

Harvesting: partitioning of singlets and triplets

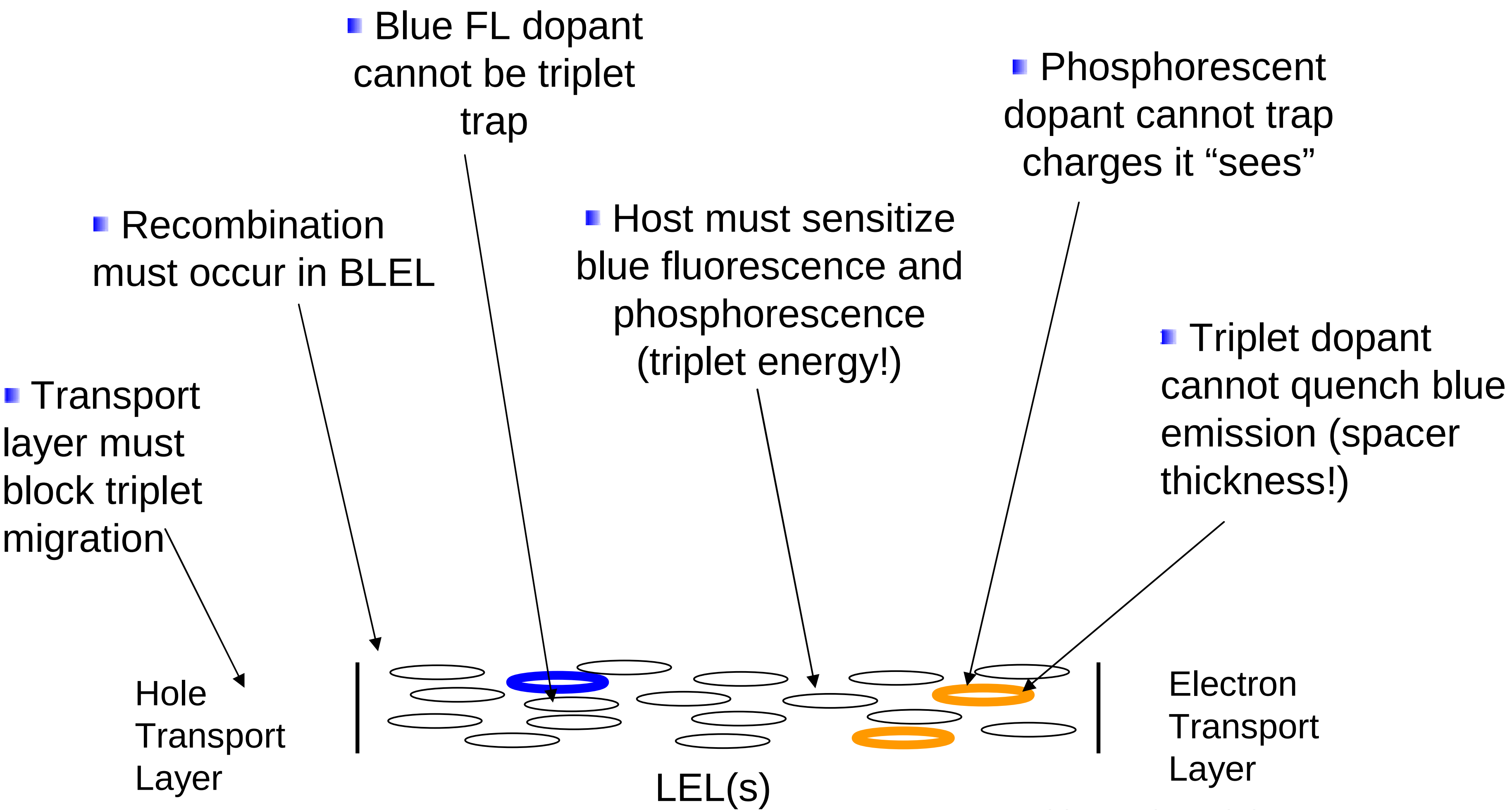


Y.Sun et al., Nature ***440****, 908 (2006)*

<u>Harvesting hybrid device:</u>

- ❑ Phosphorescent green and red
- ❑ Fluorescent blue dopant
- ❑ Recombination in fluorescent EML only, forms singlets and triplets
- ❑ Singlets harvested immediately by blue fluorescent dopant
- ❑ “Blue” triplets diffuse (Dexter transfer) to triplet EML(s) where harvested by phosphorescent dopant(s)
- ❑ In principle: 100% IQE?

Harvesting requires complex materials/architecture design

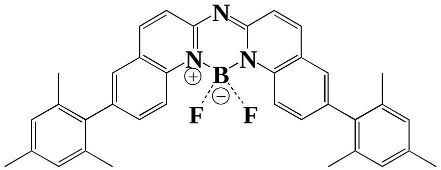


- Blue FL dopant cannot be triplet trap
- Phosphorescent dopant cannot trap charges it “sees”
- Recombination must occur in BLEL
- Host must sensitize blue fluorescence and phosphorescence (triplet energy!)
- Triplet dopant cannot quench blue emission (spacer thickness!)
- Transport layer must block triplet migration

Kondakova et al, J.Appl.Phys., 107, 014515, 2010

Blue fluorescent emitter

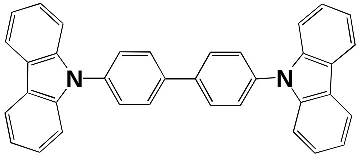
Triplet energy of emitter is a critical parameter to enable triplet diffusion mechanism



MQAB

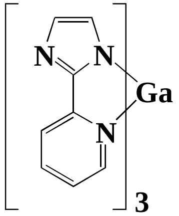
E_S=2.82 eV

E_T=2.55 eV



CBP

E_T=2.61 eV



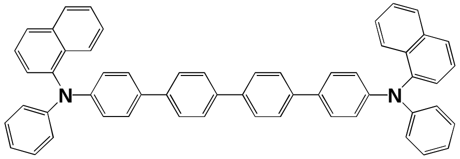
Ga(pyimd)$_3$

E_T=2.57 eV

E_T: FL dopant $\geq$ FL host $\geq$ spacer

E_T: FL host (CBP) ~ FL dopant (MQAB) $\geq$ spacer (Ga(pyimd)$_3$)

Kondakova et al, J.Appl.Phys., 107, 014515, 2010



E_S=2.91 eV

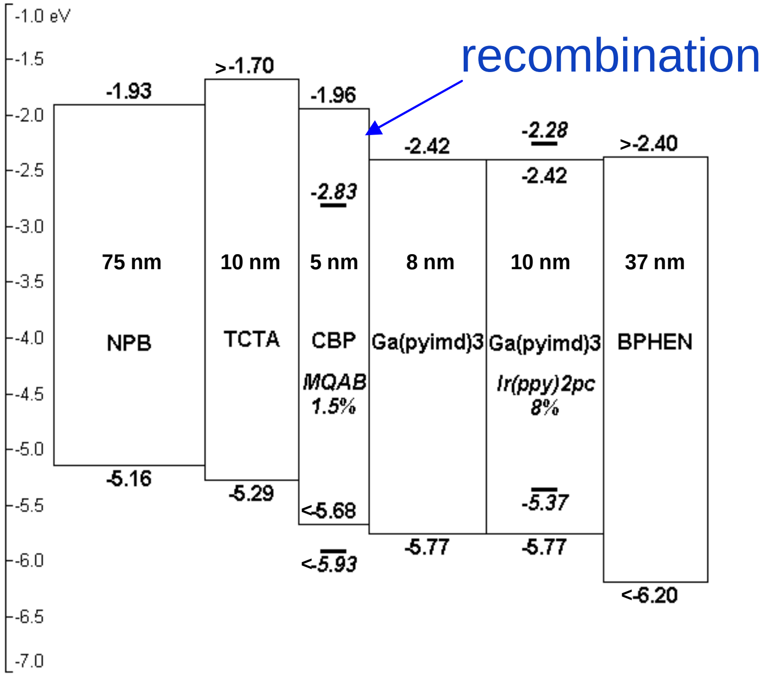
E_T=2.30eV

G. Schwartz et al., Adv.Func.Mater.,2009,19, 1319

4P-NPD

B|Y Hybrid OLED, maximized for blue emission

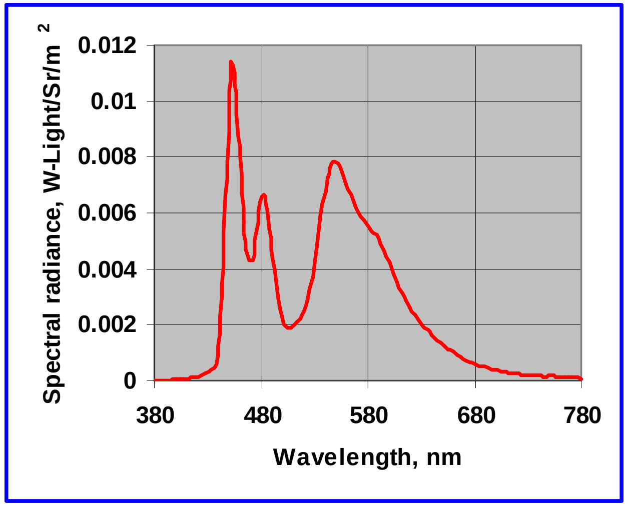
At 1000 cd/m^2 (3.2 mA/cm^2): 13.6% EQE, 34.8 cd/A, 3.8 V, 30.1 lm/W, (0.32, 0.36)



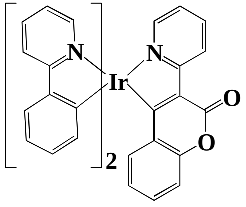
HTL	EBL	BLEL	spacer	YLEL	ETL
75 nm	10 nm	5 nm	8 nm	10 nm	37 nm

Spacer prevents Förster transfer $^1\Psi$, allows Dexter transfer $^3\Psi$

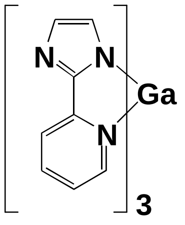
Kondakova et al, SID'08
Kondakova et al, J.Appl.Phys., 107, 014515, 2010



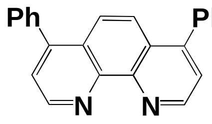
at 1 mA/cm^2



Ir(ppy)$_2$pc



Ga(pyimd)$_3$

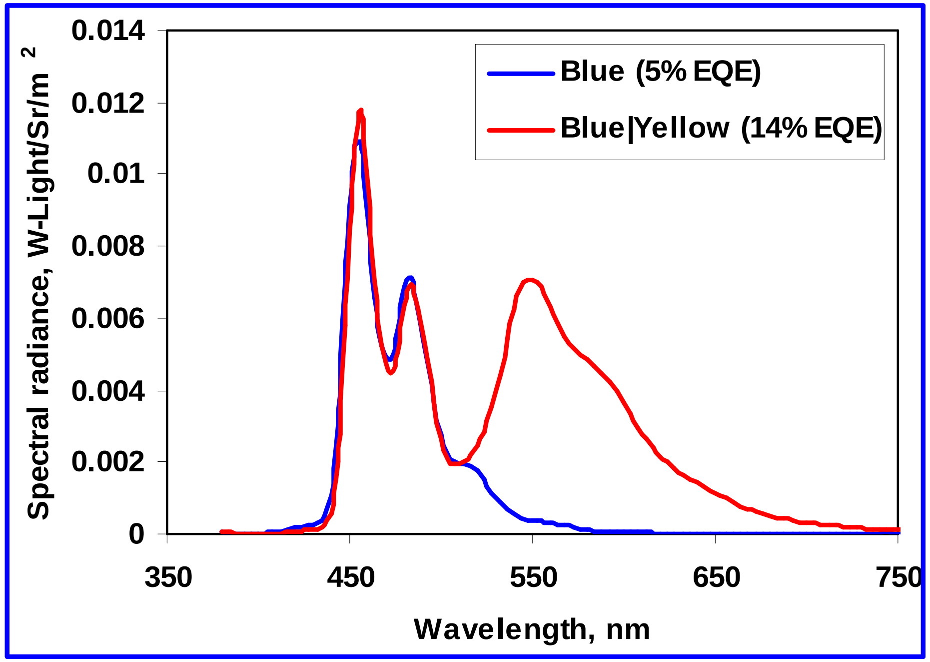


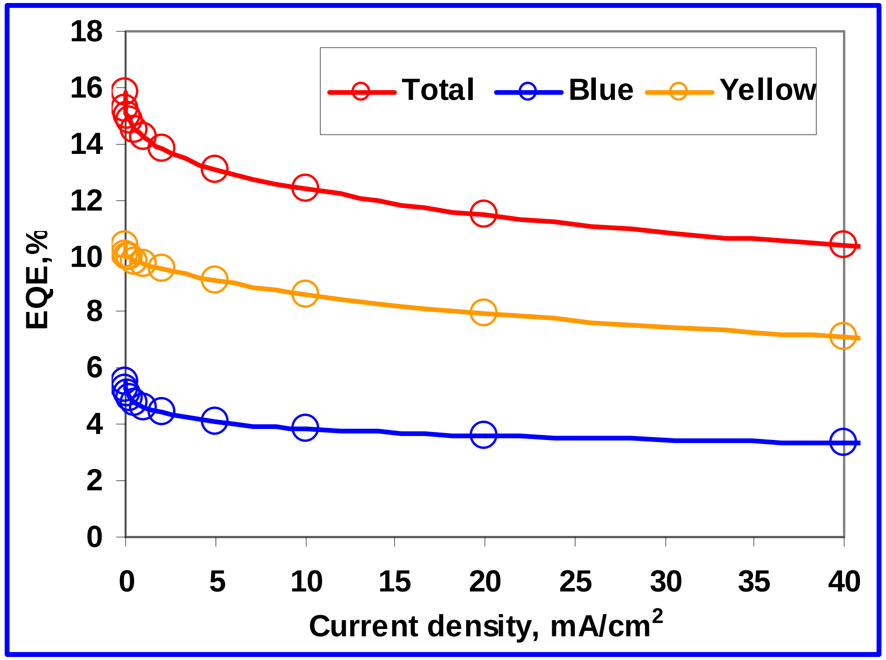
Bphen

Efficiency analysis of Blue and Yellow emission components in B|Y hybrid OLED

Proof of Harvesting

Spectra at 1 mA/cm^2





Very efficient fluorescence
Fluorescence remains
Phosphorescence appears

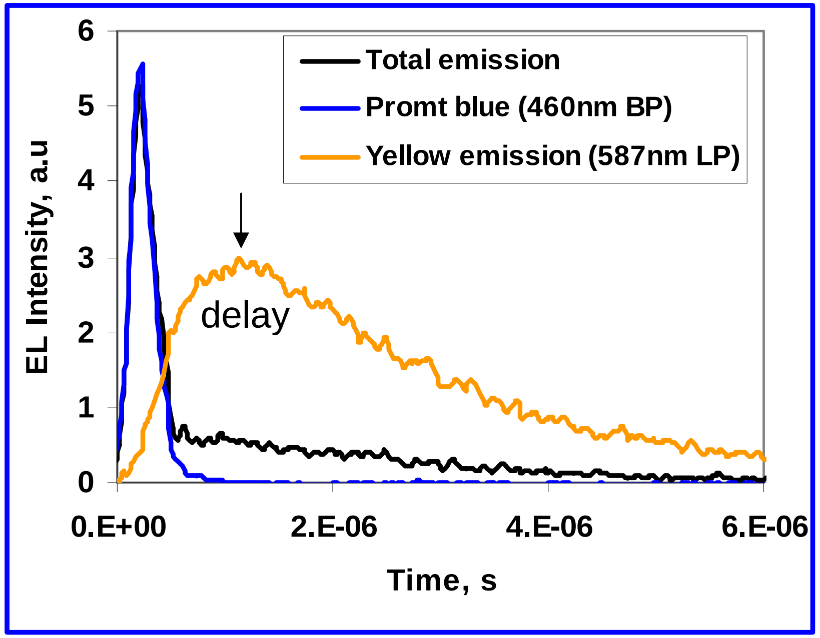
Fluorescence decreases faster at small currents (0.01-10 mA/cm^2)

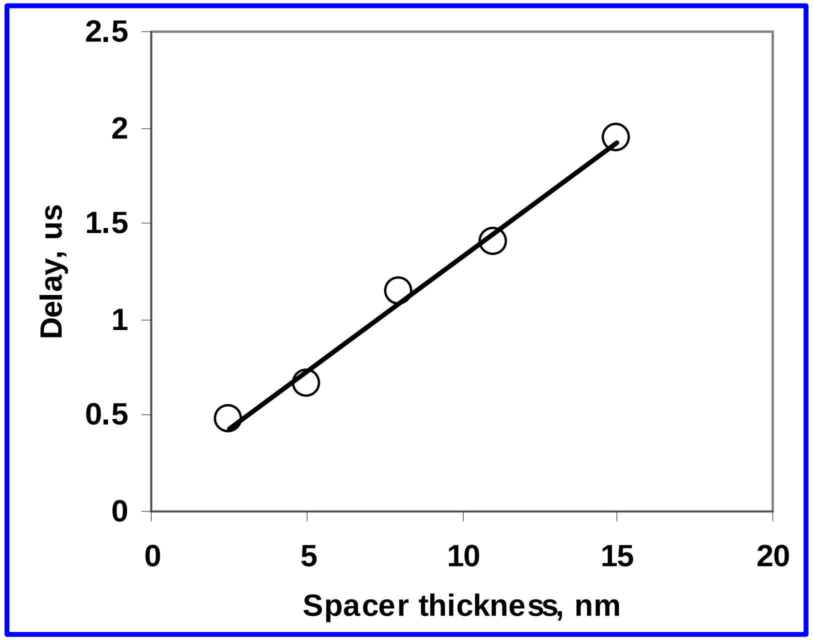
Kondakova et al, SID'08

Time-resolved electroluminescence of B|Y Hybrid

Proof of harvesting

Voltage pulse 2 µs +5.4 V, –10 V





- ~1 µs delay (spacer of 8 nm) between maxima of blue and yellow emission after voltage pulse
- Singlet and triplet excitons harvested separately → triplet exciton diffusion

Kondakova et al, SID'08
Kondakova et al, J.Appl.Phys., 107, 014515, 2010

Harvesting hybrid white OLEDs

- ❑ Blue|Yellow, Blue|Red, B|G|R, and stacked (BR||BG) hybrid devices operating by harvesting mechanism (triplet exciton diffusion) were demonstrated

Device	% EQE	**V**	**Lm/W**	**CIE x,y**
BY	13.6	3.8	30.1	0.317, 0.364
RGB	12.6	4.0	21.4	0.317, 0.317
BR||BG	16.9	9.4	9.9	0.330, 0.329

- ❑ Mechanism involving triplet exciton diffusion was evidenced by:
  - ✓ Efficiency analysis of fluorescent and phosphorescent EL
  - ✓ Time-resolved EL
  - ✓ Magnetic field effect on EL
  - ✓ Electrically-detected EPR

Kondakova et al., SID'08
Kondakova et al, J.Appl.Phys., 107, 014515, 2010

Summary

- ❑ Hybrid white devices can bridge the performance gap between fluorescent and phosphorescent OLEDs achieving high power efficiency and stability;
- ❑ Phosphorescent OLED devices require complex architecture of layers; the understanding of material properties is critical for optimizing the device performance;
- ❑ Single-stack white OLEDs provide simpler structures, higher power efficacy compared to multi-stack OLEDs;
- ❑ Efficient white-emitting hybrid devices operating by harvesting mechanism (exciton diffusion) have been demonstrated, the triplet diffusion mechanism was evidenced by various physical methods.

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Manufacturing OLED Lighting Panels
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