전자물리특강-OLED

White OLEDs for displays and lighting

Changhee Lee
School of Electrical Engineering and Computer Science
Seoul National Univ.
chlee7@snu.ac.kr

Brief history of Lighting

- 500,000 years ago – fire, 1st torch
- 70,000 years ago – 1st lamp (wick)
- 1,000 BC – 1st candle
- 1772 gas lighting

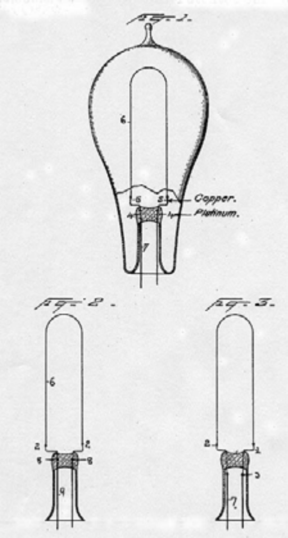
pyroluminescence

- 1879 T. A. Edison, incandescent filament lamp: Dawn of electric lighting.
- 1907 H. J. Round, 1st LED (SiC), Electrical World 49, 309 (1907)
- 1910 P. Claude, discharge lamps filled with inert gases
- 1938 GE and Westinghouse Electric Co. white fluorescent lamps.
- 1962 N. Holonyak Jr. and Bevaqua, GaAsP (visible light – red)
- 1987 C. W. Tang, OLED (Alq_3, Green)
- 1995 S. Nakamura et al, GaInN LED (blue & Green)

History of Lighting
(http://lighting.sandia.gov/)

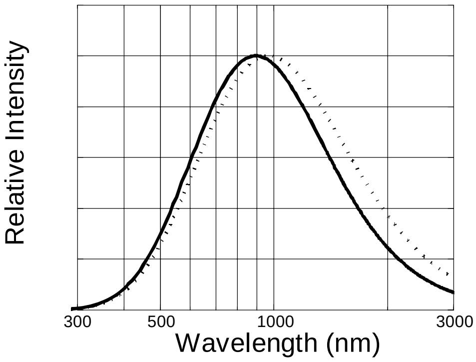
More Efficient, Convenient

Incandescent Lamp



Edison's US. Patent No. 444,530 (issued Jan 13, 1891)

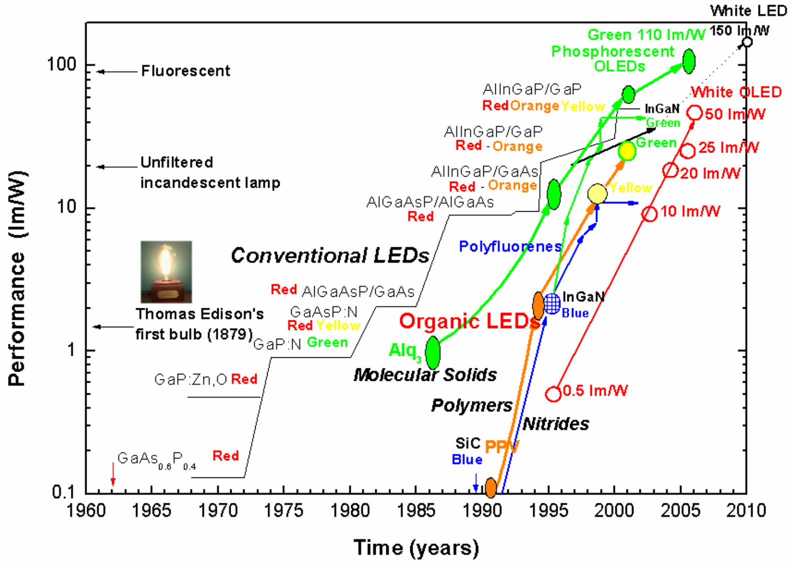
black body (dot) and tungsten radiator (solid line) at 3000 K



Now, Lifetime ~ 2000 h
Efficiency ~ 17 lm/W

Evolution of OLED Performance

Updated the data in J. R. Sheats *et al.*, Science **273**, 884 (1996).



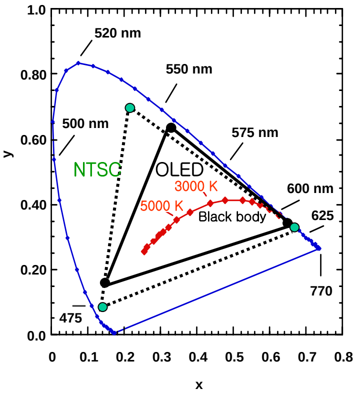
SEC
40" WXGA
a-Si AMOLED

Mass production of
AMOLED
Samsung SDI

Performance of RGB OLED Devices

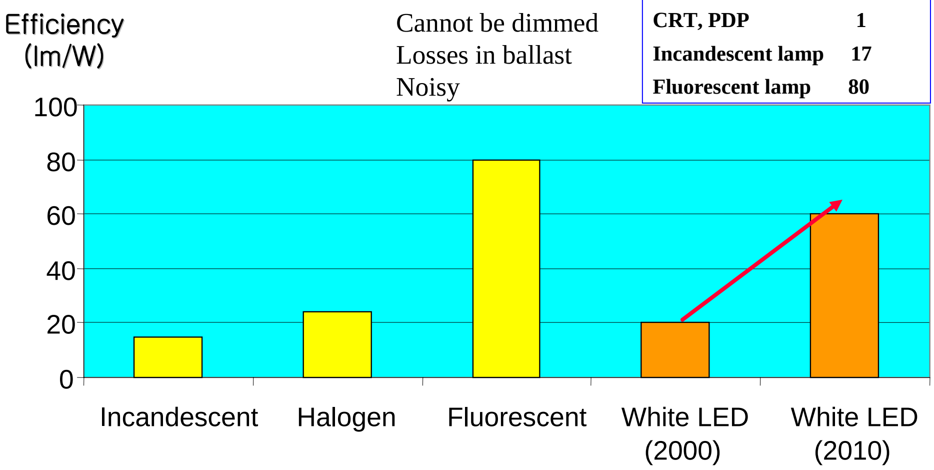
Color			CIE (x,y)	Efficiency (cd/A)	Half-Life (hr)
저분자	형광	Red	0.65, 0.35	5.5	>80,000 @ 1000 cd/m^2
		Green	0.32, 0.62	19	40,000 @ 1000 cd/m^2
		Light blue	0.17, 0.30	12	21,000 @ 1000 cd/m^2
		Blue	0.15, 0.15	5.9	7,000 @ 1000 cd/m^2
		White	0.30, 0.34	12	23,000 @ 1000 cd/m^2
	인광	Red	0.65, 0.35	15	>22,000 @ 500 cd/m^2
		Orange	0.61, 0.38	22	15,000 @ 300 cd/m^2
		Green	0.31, 0.64	27	25,000 @ 600 cd/m^2
		Light blue	0.14, 0.23	8	-
		White	0.39, 0.39	38	-
고분자	형광	Red	0.68, 0.32	1.7	1790 @ 1000 cd/m^2
		Orange	0.58, 0.42	0.9	8138 @ 1000 nit
		Yellow	0.50, 0.49	2.1	2420 @ 4000 cd/m^2
		Green	0.43, 0.55	7.7	2912 @ 2000 cd/m^2
		Blue	0.16, 0.22	6.9	>1147 @ 800 cd/m^2
		White	0.30, 0.33	3.8	235 @ 800 cd/m^2
	인광	Red	0.67, 0.28	1.3	>8350 @ 100 cd/m^2
		Green	0.36, 0.59	22.8	2649 @ 400 cd/m^2

OLED의 색좌표



Solid State Lighting

Luminous Efficiency (lm/W)	
OLED	**10 +**
LCD screen	**1.5**
CRT, PDP	**1**
Incandescent lamp	**17**
Fluorescent lamp	**80**

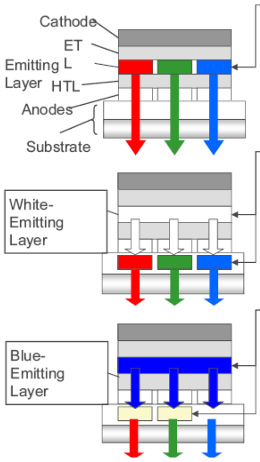


Flickers
Cannot be dimmed
Losses in ballast
Noisy

Ref. A. Zukauskas, M. S. Shur, R. Caska, Introduction to Soild-State Lighting

White Organic Light-Emitting Devices

- Full-Color Display
- Backlight of TFT-LCD
- Lighting – Light signs, decorative lighting, glowing wall paper, ceilling lights, etc.



I. Patterned-Emitting Layer

Advantages
- High efficiency
- Good color

Disadvantages
- Aperture ratio issues
- Typically uses shadow masking for RGB patterning
- Differential aging of RGB

II. White-Emitting Layer with Color-Filter Array

Advantages
- Unpatterned emitting layer (no masks)
- Aperture ratio not affected by RGB patterning
- Enabled by high-efficiency white

Disadvantages
- Loss of efficiency is due to filter absorption

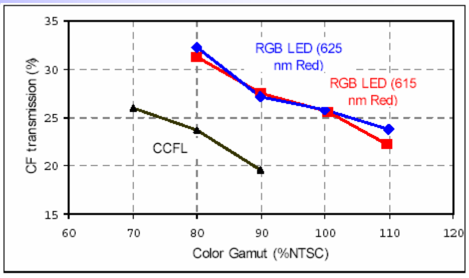
III. Blue-Emitting Layer with Color-Change Medium

Advantages
- Unpatterned emitting layer (no masks)

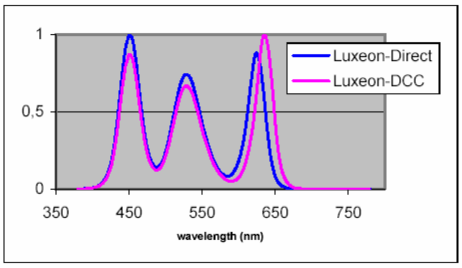
Disadvantages
- Requires high efficiency blue
- Blue stability typically poorest
- Compatibility of CCM materials

LED backlighting

Advantages of using LEDs over conventional light sources such as CCFL:
- long life
- ruggedness
- high frequency dynamical operation
- Hg-free light source
- Better color gamut



	Dominant Wavelength (nm)	Efficacy (Lm/W, 25°C)
Red in Luxeon-DCC	625	55
Red in Luxeon-Direct	617	60
Green	533	46
Blue	452	5.5
RGB-White	-	37
White (phosphor-converted)	-	35



Wiep Folkerts (Lumileds Lighting), SID 04 Digest, p. 1226

Issues of Solid State Lighting

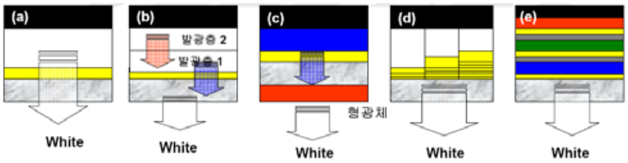
- Improve efficiency of light generation
- Improve efficiency of light extraction
- Improve quality of light
- Reduce cost

Methods of Making White LEDs

- Wavelength Conversion
  1. Blue LED with phosphors
  2. UV LED with several phosphors
- Color Mixing
  3. Two or more emitting layers of different colors.
     - white light with a high color rendering index (CRI).
     - relatively easy to change the hue for different applications.

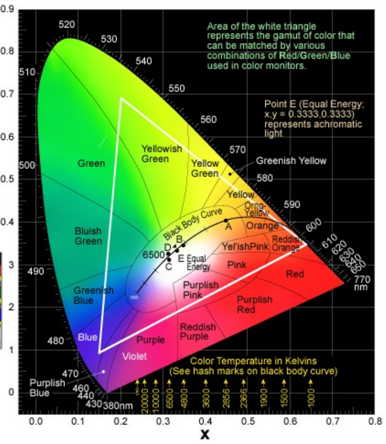
R+G+B=W

R + C = W G + M = W B + Y = W



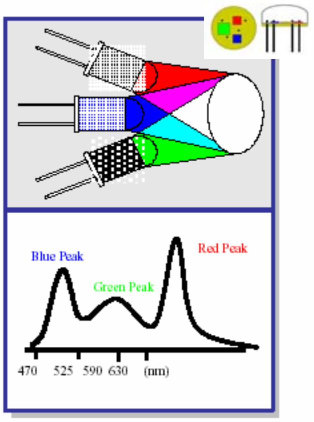
OLED NET

그림 7.백색OLED 제조방식; (a)단층발광, (b)다층발광, (c) 색변환방식, (d) Microcavity 방식, (e) 소자적층방식



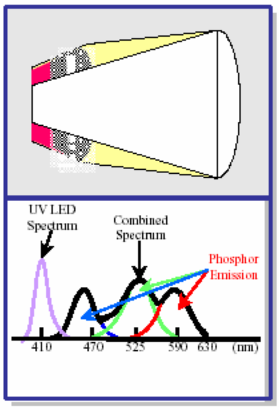
백색 LED 소자

Red + Green + Blue LEDs



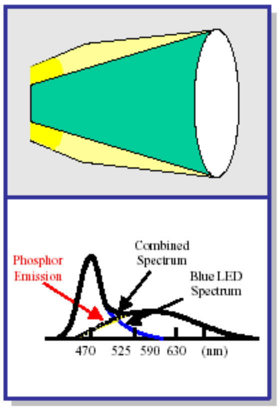
RGB LEDs

UV LED + RGB Phosphor



UV LED + RGB phosphor

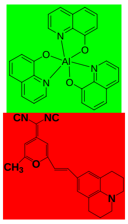
Binary Complimentary



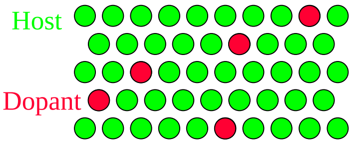
Blue LED
+
Yellow phosphor

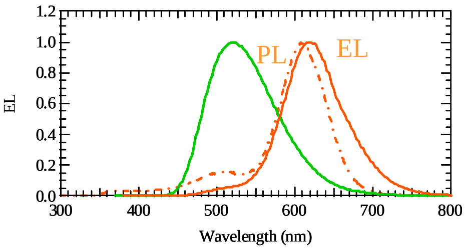
Energy transfer & Carrier trapping

Alq3

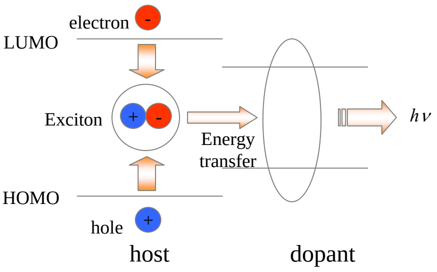


DCM2

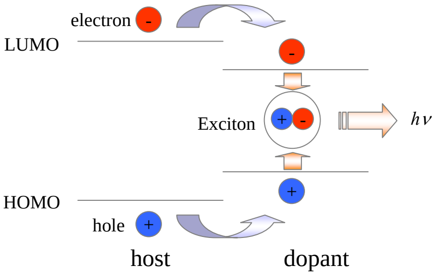




Energy transfer



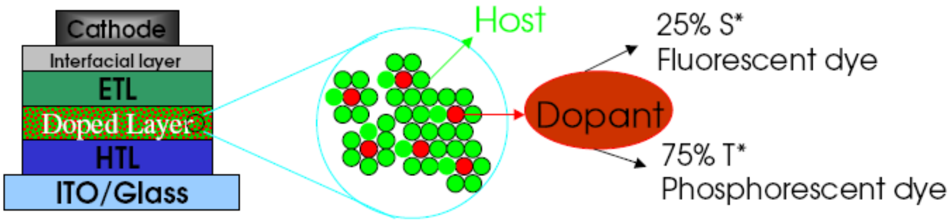
Direct trapping



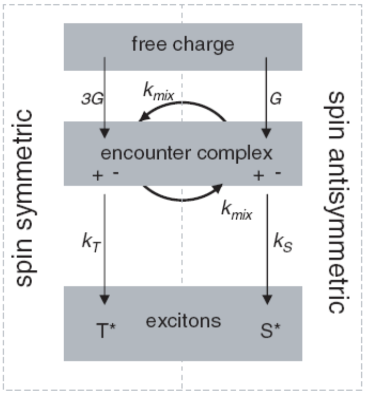
Doping in OLEDs

- Doping fluorescent dyes
  C. W. Tang, S. A. VanSlyke, and C. H. Chen, J. Appl. Phys. **65**, 3610 (1989)
- Doping phosphorescent dyes
  M. A. Baldo, et al, Nature 395, 151 (1998)
- Effects of doping:

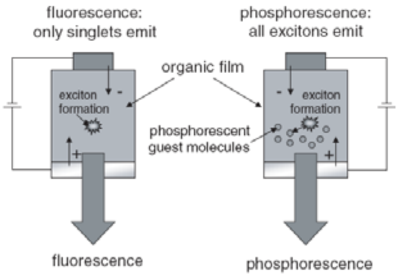
1. Color tuning.
2. Increase the device quantum efficiency
3. In general, the doped layer is more thermally stable than the undoped layer (increase of entropy).
4. Proper dopants can increase the operational lifetime of the device.



Exciton formation



If $k_S > k_T$, $\chi_S > ¼$
If $k_S < k_T$, $\chi_S < ¼$
If $k_{mix} = 0$, $\chi_S = ¼$



χ_S ~ fluorescence/phosphorescence

Caution for this simple method:

(1) It is necessary to correct for the differing photoluminescent efficiencies of the fluorescent and phosphorescent guest molecules.

(2) The efficiency of energy transfer to both guest materials must be determined to ensure that radiative emission accurately reflects the number of excitons formed within the device.

(3) The impact of quenching phenomena must be calculated for both singlet and triplet excitons.

(4) When applied to polymeric systems, it is especially important to ensure that excitons are formed on the polymeric host and not on the small molecularweight phosphorescent guest.

M. Baldo and M. Segal, phys. stat. sol. (a) 201, 1205 (2004)

Fluorescent Dye doping

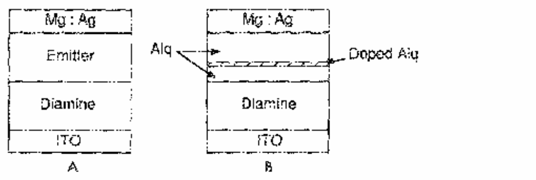


FIG. 1. Configurations of multilayer organic EL cells: (a) ITO/diamine/doped or undoped Alq/Mg:Ag, (b) ITO/ diamine/Alq/doped Alq/Alq/Mg:Ag.

C. W. Tang and S. A. VanSlyke, C. H. Chen,
J. Appl. Phys. **65**, 3610 (1989)

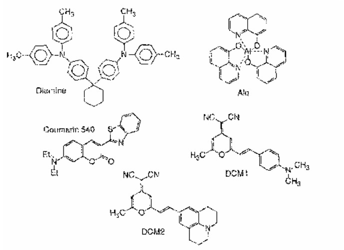


FIG. 2. Molecular structures of (1) diamine, (2) Alq, and (3) C540, DCM1, and DCM2.

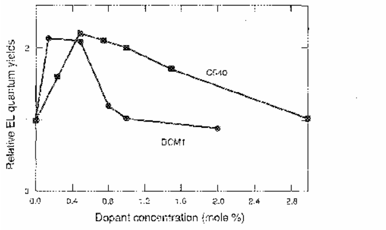
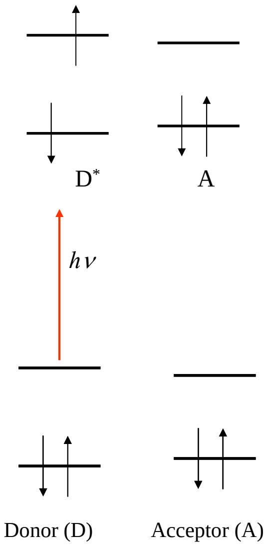


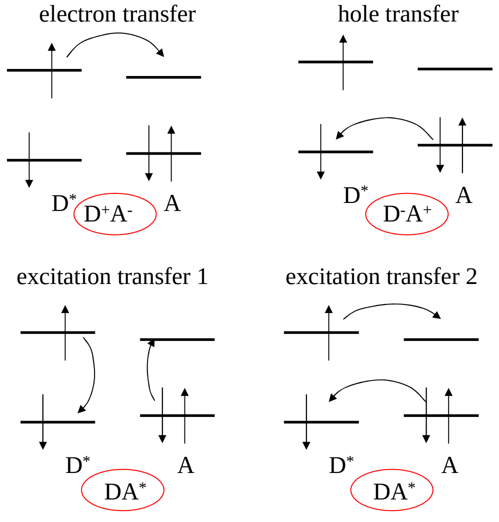
FIG. 10. Relative EL quantum efficiencies as a function of dopant concentration in Alq.

Excitonic interaction and excitation transfer



Excitation

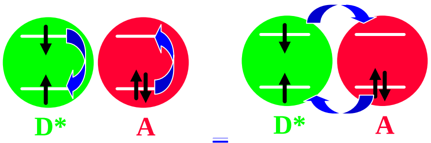
Excitation and energy transfer



Förster: overlap of spectra, dipole interaction
Dexter: overlap of wavefunctions

Energy Transfer Processes

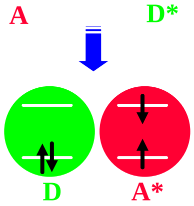
Förster excitation transfer (Dipole-Dipole Excitation Transfer)



Dexter excitation transfer (electron exchange excitation transfer)

Forster energy transfer

$$k_{D\to A} = \frac{K^2 J\, 8.8\times 10^{-28}\ \text{mol}}{n^4 \tau_o r^6}$$



Dexter energy transfer

$$k_{ET} \propto \frac{h}{2\pi} P^2 J \exp\ (-2r/L)$$

$$\text{Overlap integral}: J = \int \frac{\varepsilon_A(\tilde{\nu})\cdot F_D(\tilde{\nu})}{\tilde{\nu}^4} d\tilde{\nu}$$

$$W_{DA} = k_r^D \left(\frac{R_0}{R}\right)^6 \quad R_0^6 = 8.8\cdot 10^{17}\cdot \frac{\kappa^2}{n^4}\cdot \int \frac{\varepsilon_A(\tilde{\nu})\cdot F_D(\tilde{\nu})}{\tilde{\nu}^4} d\tilde{\nu}$$

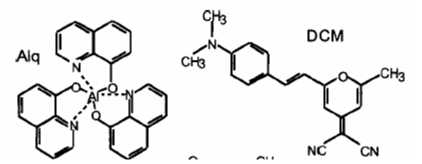
For photosynthetic systems R is typically 1 nm, R_0 is typically 8 nm,

$k_r^D \approx 5\cdot 10^7 s^{-1} \to W_{DA} \approx 10^{13} s^{-1}$

Förster radius

Excitation dynamics of dye doped tris(8-hydroxy quinoline) aluminum films

K. Read, H. S. Karlsson, M. M. Murnane and H. C. Kapteyn, R. Haight, J. Appl. Phys. 90, 294 (2001)



$$R_0^6 = \frac{0.5291\kappa^2}{n^4 N_A}\cdot \int \frac{\varepsilon_A(\tilde{\nu})\cdot F_D(\tilde{\nu})}{\tilde{\nu}^4} d\tilde{\nu}$$

κ=donor/acceptor orientation factor;
$\kappa^2 = 2/3$ for a randomly deposited film
N_A is Avogadro's number
n=1.7 for Alq3
R_o = 31 Å

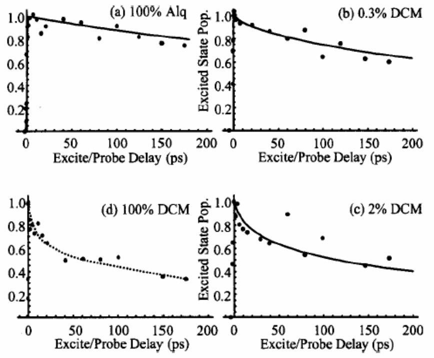
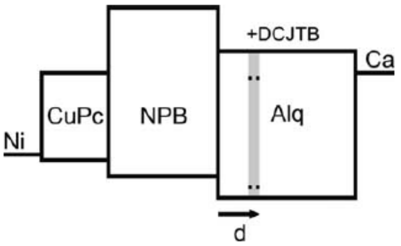
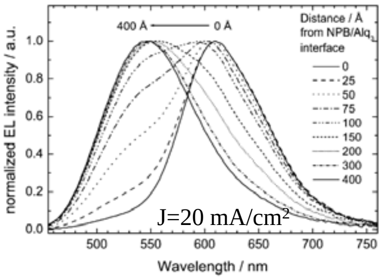


FIG. 3. Excited state population as a function of excite/probe delay for the sample compositions (a) 100% Alq, (b) Alq+0.3%DCM, (c) Alq +2%DCM, and (d) 100% DCM. The 100% DCM sample was excited with 68 μJ/cm^2, and all others were excited with 91 μJ/cm^2 (1.8 $\times 10^{27}$ phot/cm^{2}s) of 90 fs 3.14 eV laser pulses. The solid curve, (a) represents bimolecular singlet annihilation. The solid curves, (b) and (c), are from fits including excitation transfer, excimer formation, and stimulated emission. The dotted curve, (d), is only a guide to the eye.

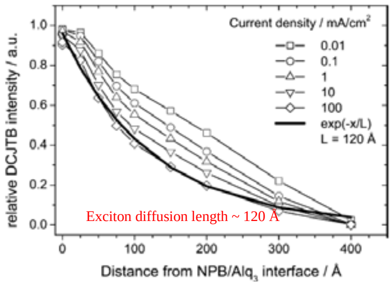
Location and extent of the recombination and emission zone



Schematic energy level diagram of delta-doped devices having a 25 Å Alq3/DCJTB (1%) sensing layer at various positions (d) in the Alq3 layer. The device structure is Ni/CuPc (150 Å)/NPB (500 Å)/Alq3 (500 Å)/Ca (200 Å).



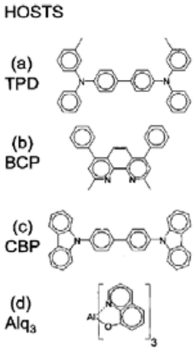
J=20 mA/cm²

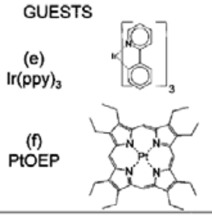


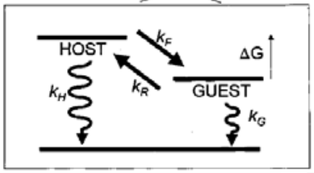
Exciton diffusion length ~ 120 Å

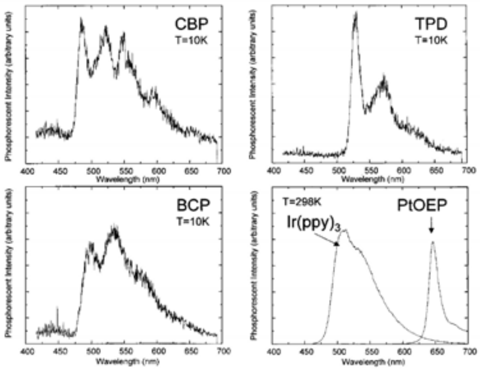
T.A. Beierlein, B. Ruhstaller, D.J. Gundlach, H. Riel, S. Karg, C. Rost, W. Rieß, Synth. Met. 138, 213 (2003)

Triplet energy of R & G phosphors







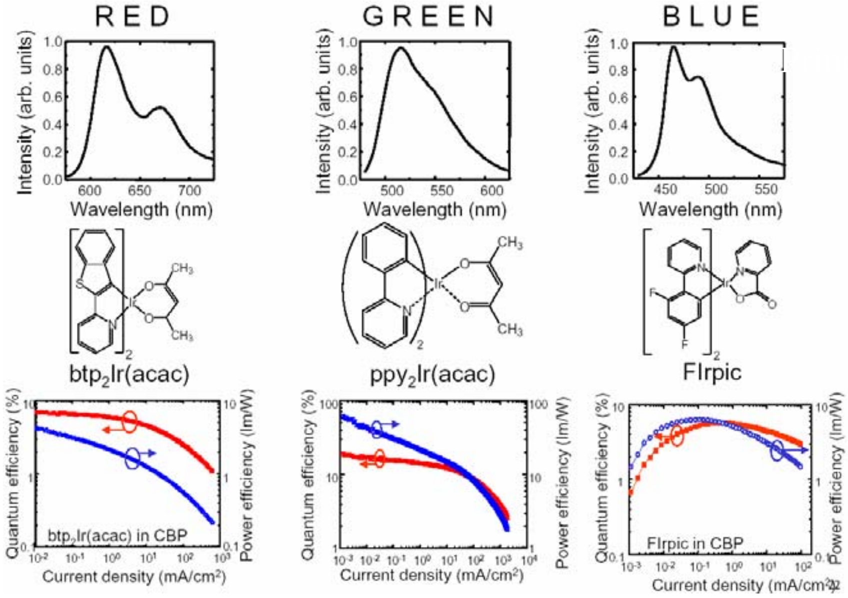


Material	Triplet energy ($\pm$0.1 eV)	Triplet lifetime
PtOEP	1.9	110$\pm$10 μs[a]
Ir(ppy)3	2.4	0.8$\pm$0.1 μs[b]
CBP	2.6	>1 s
BCP	2.5	<10 μs
TPD	2.3	200$\pm$50μs
Alq_3[c]	2.0	25$\pm$15 μs

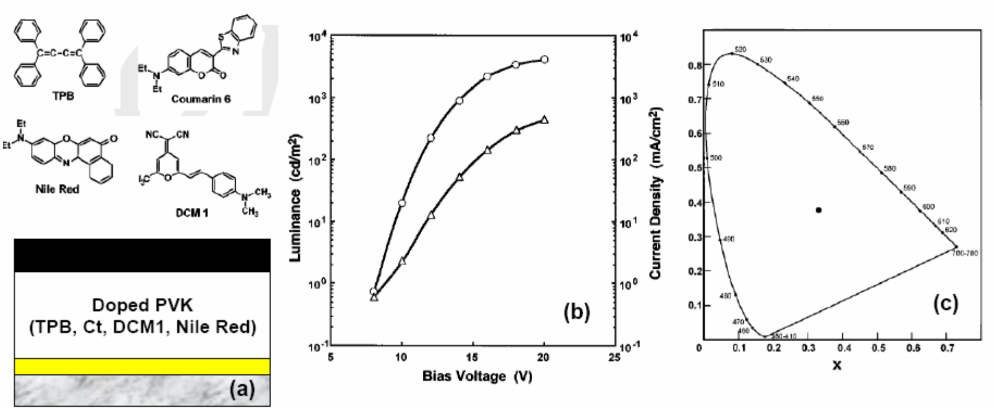
Guest (lifetime)	Host	ΔG ($\pm$ 0.1 eV)	Host lifetime	Emission lifetime (μs)	Trapping on guest	EL quantum efficiency
PtOEP (110$\pm$10 μs)	CBP	−0.7	>1 s	80$\pm$5	Yes	6%
	$Ir(ppy)_3$	−0.5	<0.1 μs	80$\pm$5	?	3%
	TPD	−0.4	200$\pm$50 μs	80$\pm$5	Yes	3%
	Alq_3	−0.1	25$\pm$15 μs	40$\pm$5	No	3%
$Ir(ppy)_3$ (0.8$\pm$0.1 μs)	CBP	−0.2	>1 s	0.4$\pm$0.05	Yes	8%
	TPD	+0.1	200$\pm$50 μs	15$\pm$2	No	3%
	Alq_3	+0.4	25$\pm$15 μs	<0.1	?	<0.1%

M. A. Baldo and S. R. Forrest, Phys. Rev. B 62, 10958–10966 (2000).

Organic Electrophosphorescence devices



Single emitting layer

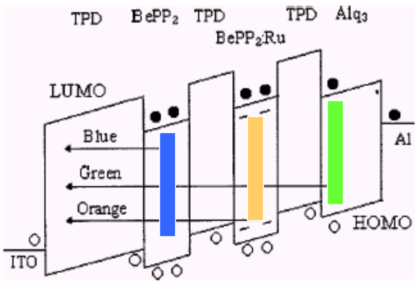


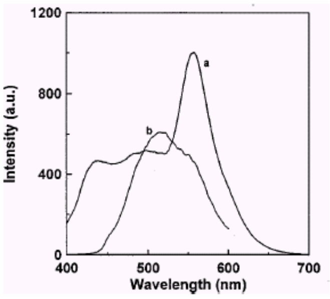
Kido, APL (2005)

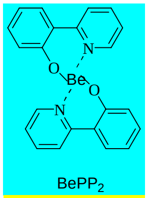
Multi-Quantum Well Structure

1. The confinement of charge carriers in light-emitting quantum wells can enhance the forming probability of excitons and the light-emitting efficiencies of the devices.
2. Compared with multi-layer white OLEDs, the influence of band gap matching can be negligible, and the positions of different color light-emitting quantum wells can be exchangeable.
3. Easy turning of Commission International de I'Eclairange (CIE) chromaticity

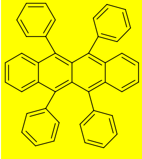
0.41 lm/W, (0.32, 0.38) at 9V







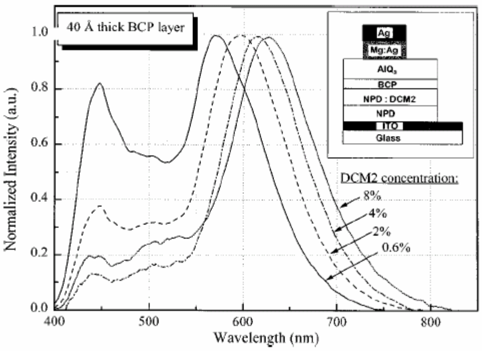
BePP$_2$

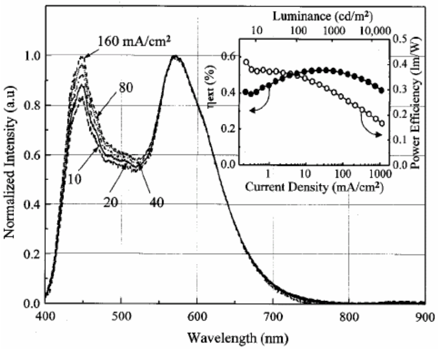


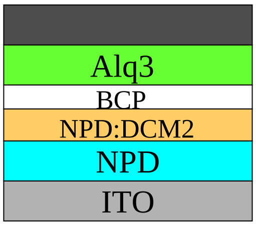
Rubrene

Z. Y. Xie (Jilin U), *Appl. Phys. Lett.*, **74**, 1999, 641

Complementary Color Stack






Alq3
BCP
NPD:DCM2
NPD
ITO

Interlayer sequential energy transfer (ISET):
NPD → Alq3 → DCM2

Hole-blocking layer

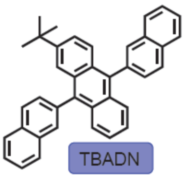
0.35 lm/W, (0.33, 0.33) , and 100 cd/ m^2 at 11..5 V

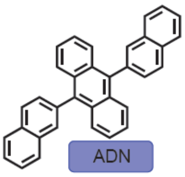
R. S. Deshpande (Princeton U.), *Appl. Phys. Lett.*, **75**, 1999, 888

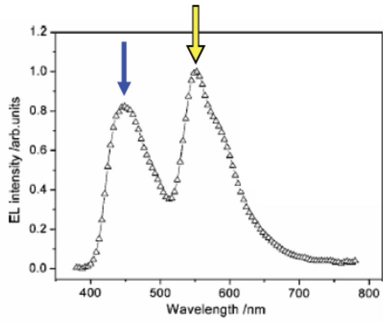
Complementary Color Stack

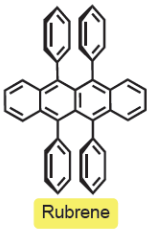
0.025% Rubrene/ 2.5% TBADN/ ADN

Device	EML	LO (cd/m^2)	QE
1	0.02% Rubrene/ ADN	17,280	1.08%
2	0.025% Rubrene/ 2.5% TBADN/ ADN	20,100	2.41%


TBADN


ADN




Rubrene

TBADN = 9,10-di-(2-naphthyl)-2-*t*-butyl-anthracene
ADN = 9,10-di-(2-naphthyl)-anthracene

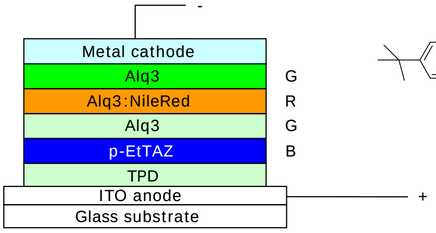
Rubrene = 5,6,11,12-tetraphenylnaphthacene

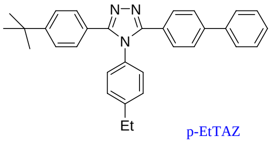
L. Wang *et al.*, *J. Appl. Phys.* **2005**, *97*, 114503.

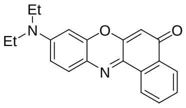
Multilayer RGB Stacks

J. Kido (Yamagata U), Science, **267**, 1995, 1332.

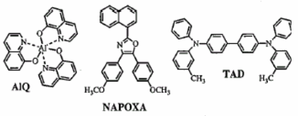
0.5 lm/W, ~ 300cd/ m^2, and (0.335, 0.415) at 12 V; 20h at 100cd/ m^2

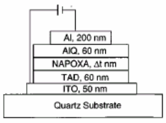


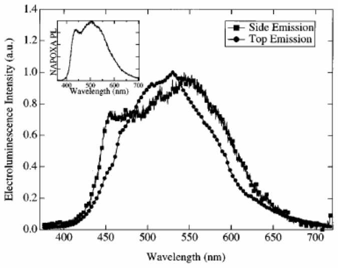

p-EtTAZ


Nile Red

R. H. Jordan (**AT&T)**, *Appl. Phys. Lett.*, **68**, 1996, 1192.



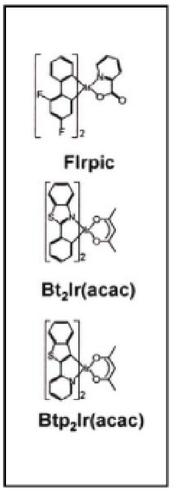




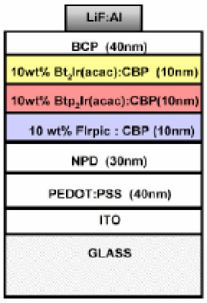
0.5 lm/ W, η_{ext}=0.7 %, CIE (0.31, 0.41), and 105 cd/ m^2 at 12 V

ITO/ TAD (600 Å)/ NAPOXA (150 Å)/Alq$_3$ (300 Å)/ Alq$_3$ (200 Å)+ DCM1 (0.3 %)/ Alq$_3$ (200 Å)/ Al (2000 Å)

RGB white OLEDs: Phosphorescence

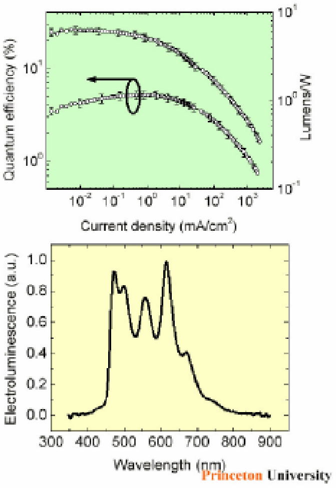


Efficient, Color Balanced WOLED



CIE = (0.37, 0.40), CRI = 83

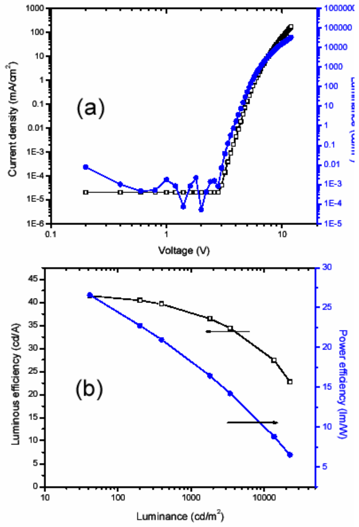
- Max luminance 31,000 cd/m² at 14V
- η_{ext} = 5.2 %, η_p = 6.4 lm/W

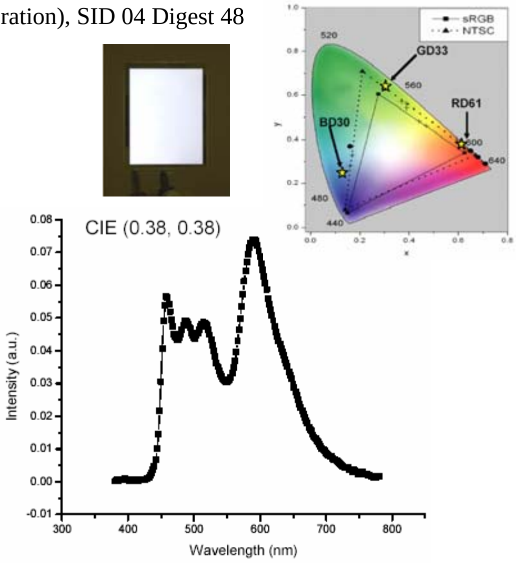


S. R. Forrest et al., Adv. Mater. **14**, 1035 (2002)

White Phosphorescent OLEDs

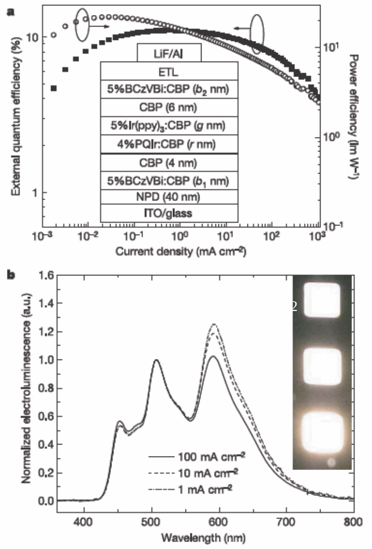
Yeh-Jiun Tung et al. (Universal Display Corporation), SID 04 Digest 48





38 cd/A, 18.4 lm/W and 16% EQE with CIE of (0.39, 0.39) at 1000 cd/m2

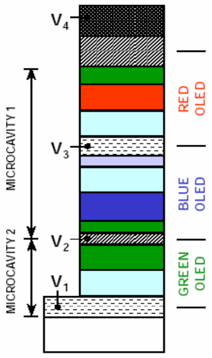
High efficiency white OLEDs



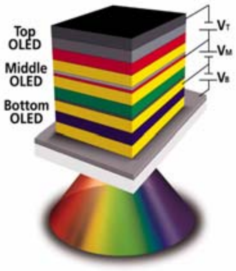
Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson, S. R. Forrest, Nature **440**, 908 (2006)

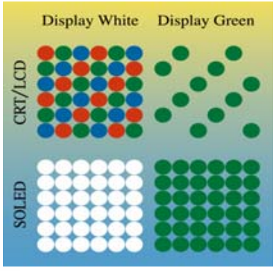
General Electric
15 lm/W (2 ft. x 2 ft.) @ 1200 lumen

Full-Color Method – Stacked OLED



MATERIAL	THICKNESS [Å]	n
Ag	1000	----
Mg:Ag	1000	----
Alq_3	170	1.72
3% DCM2 in Alq_3	330	1.72
α-NPD	540	1.78
ITO	490	2.02
CuPc	80	1.5+0.8i
α-NPD	250	1.77
Alq'_2OPh	390	1.66
Alq_3	50	1.72
Mg:Ag	80	----
Alq_3	540	1.72
α-NPD	445	1.77
ITO	1600	1.8
Glass	~1 mm	1.45



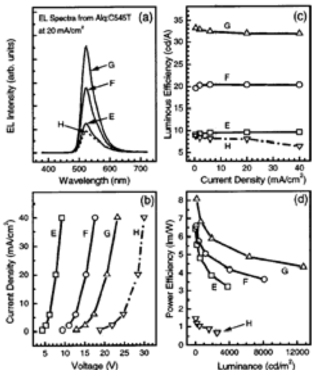


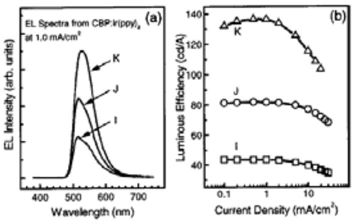
High resolution but very difficult process (fabrication of electrodes)

High-efficiency tandem OLED

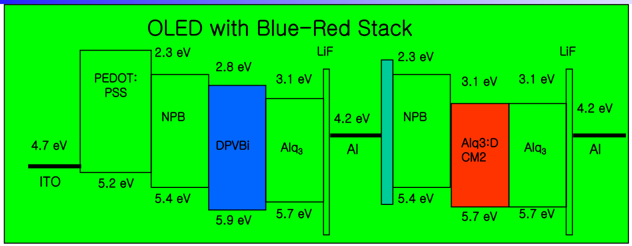
TABLE I. Layer structures of the OLED devices

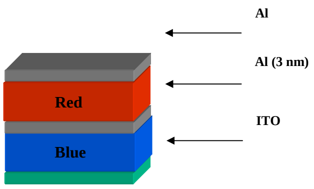
Device or unit	Layer structure
Device A	ITO/SA1/**EL-G**/OC1/**EL-R**/SC1/Mg:Ag
Device B	ITO/SA1/**EL-G**/**EL-R**/SC1/Mg:Ag
Device C	ITO/SA1/**EL-G**/SC1/Mg:Ag
Device D	ITO/SA1/**EL-R**/SC1/Mg:Ag
SA1	NPB (50 nm)
EL-G	NPB (25 nm)/Alq (20 nm)/Alq (5 nm)
OC1	Alq:Li (25 nm)/NPB:$FeCl_3$ (60 nm)
EL-R	NPB (25 nm)/Alq:DCJTB (20 nm)/Alq (5 nm)
SC1	Alq (35 nm)
Device E	ITO/SA2/**EL2**/SC2/Mg:Ag
Device F	ITO/SA2/**EL2**/OC2/**EL2**/SC2/Mg:Ag
Device G	ITO/SA2/**EL2**/OC2/**EL2**/OC2/**EL2**/SC2/Mg:Ag
Device H	ITO/SA2/**EL2**/**EL2**/**EL2**/SC2/Mg:Ag
SA2	NPB (60 nm)
EL2	NPB (30 nm)/Alq:C545T (20 nm)/Alq (10 nm)
OC2	Alq:Li (30 nm)/NPB:$FeCl_3$ (60 nm)
SC2	Alq (30 nm)
Device I	ITO/SA3/**EL3**/SC3/Mg:Ag
Device J	ITO/SA3/**EL3**/OC3/**EL3**/SC3/Mg:Ag
Device K	ITO/SA3/**EL3**/OC3/**EL3**/OC3/**EL3**/SC3/Mg:Ag
SA3	NPB (60 nm)
EL3	NPB (30 nm)/CBP: $Ir(ppy)_3$ (20 nm)/TPBI (20 nm)
OC3	Alq:Li (24 nm)/NPB:$FeCl_3$ (48 nm)
SC3	TPBI (40 nm)

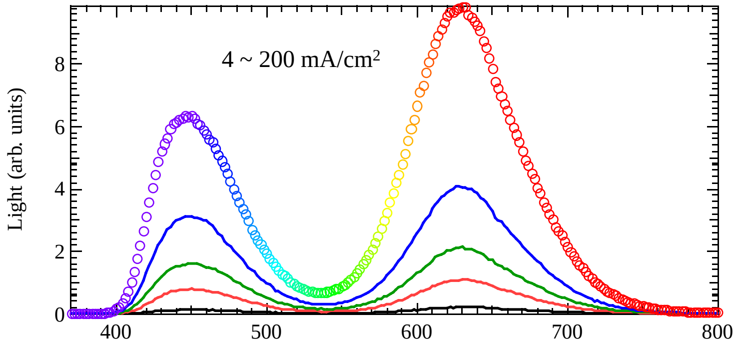




White OLEDs with multilayer stack structure





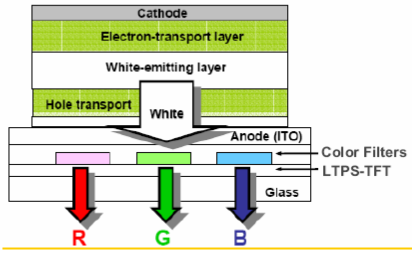


White OLED + CF

Methods of Color Patterning (White OLED + RGB Color Filters)

(Prototype (2002) Kodak/Sanyo
15″ AMOLED W-RGB

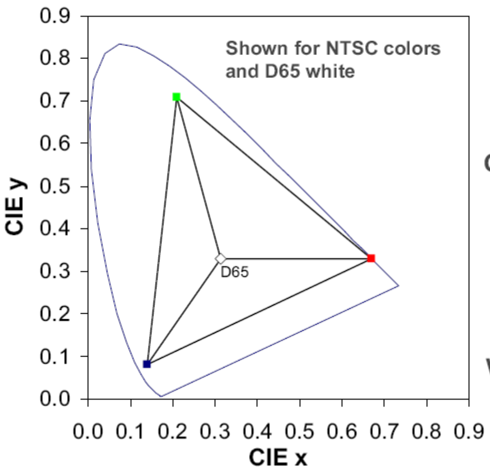
Kodak commenced R&D on white OLED materials, device, and display design several years ago.

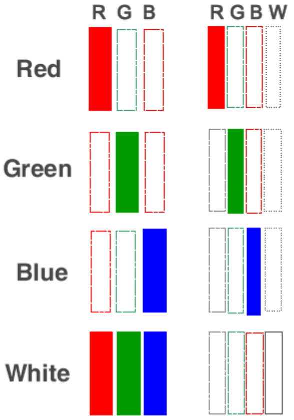


Contents	Specifications
Display size	14.7 inch
Aspect ratio	16:9
Dot Counts	1280 × RGB × 720
Dot pitch	85 × 255
Color type	RGB stripe
Contrast	>500
Thickness	1.4 mm

RGB vs RGBW

W-RGB and W-RGBW – Primary Colors

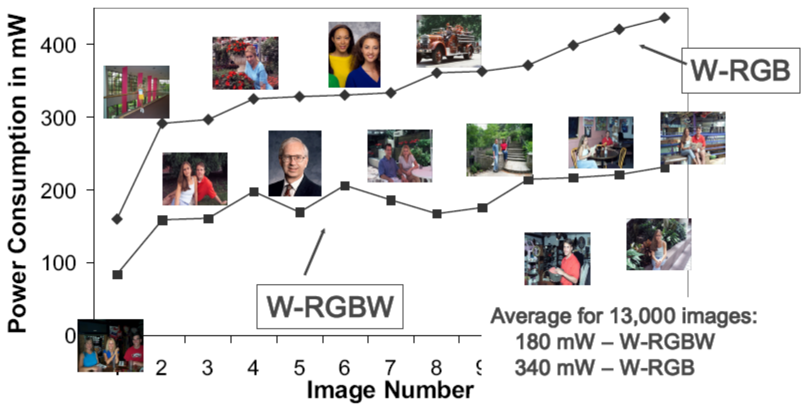




RGB vs RGBW

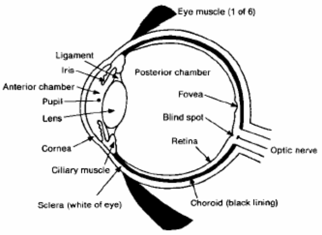
W-RGB and W-RGBW Power Consumption

2.2″ diagonal, 100cd/m^2 white after 44% T circular polarizer

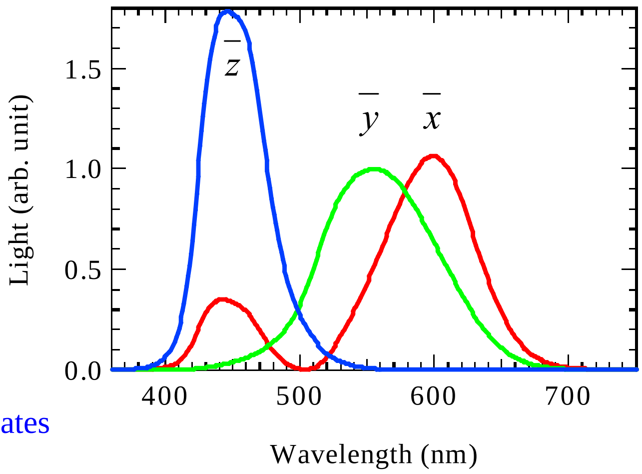


Average for 13,000 images:
180 mW – W-RGBW
340 mW – W-RGB

CIE 1931 Color Matching Functions

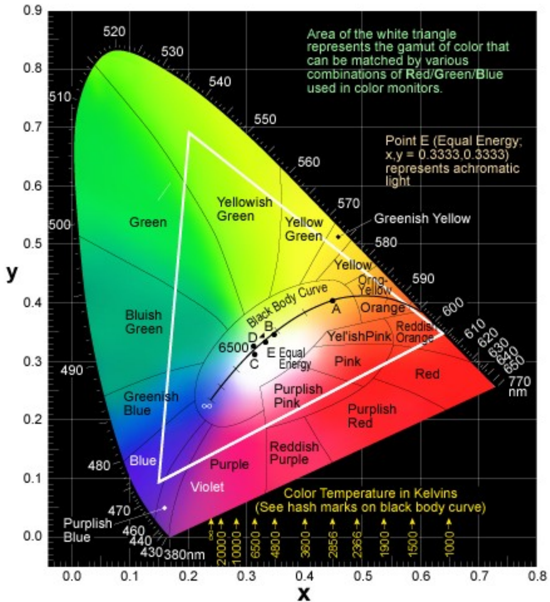


CIE 1931 Color Matching Functions (2 deg. Observer)



- Chromaticity coordinates
- Color temperature
- Color rendering index (CRI)

Chromaticity Coordinates & Color Temperature


Area of the white triangle represents the gamut of color that can be matched by various combinations of Red/Green/Blue used in color monitors.

Point E (Equal Energy; x,y = 0.3333,0.3333) represents achromatic light

Color Temperature in Kelvins (See hash marks on black body curve)

$$X = K\int_{380}^{780} S(\lambda)\bar{x}\,d\lambda \qquad K = 683\ \text{lm/W}$$

$$Y = K\int_{380}^{780} S(\lambda)\bar{y}\,d\lambda$$

$$Z = K\int_{380}^{780} S(\lambda)\bar{y}\,d\lambda$$

$$x = \frac{X}{X+Y+Z} \qquad y = \frac{Y}{X+Y+Z}$$

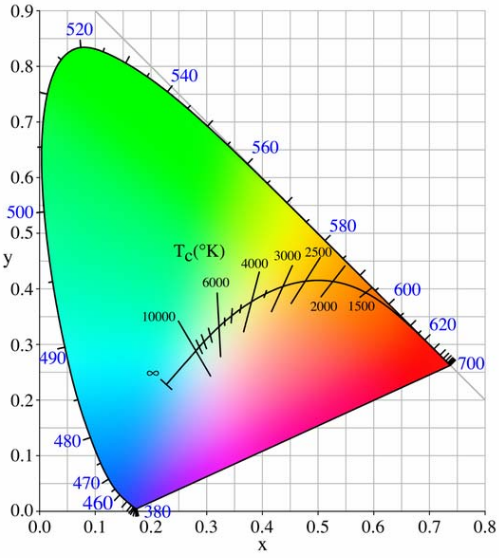
$$x + y + z = 1$$

- A black body radiator (Planckian Source) glows with a color that is solely dependent on its temperature (in K).

- Standard source

D_{65} (daylight, 6500 K)
(x,y) = (0.312, 0.329)
E = Equal Energy point: (0.333, 0.333)

Correlated color temperature



Correlated colour temperature (CCT)
= Temperature of a Planckian radiator having the chromaticity nearest the chromaticity associated with the given spectral distribution on a CIE 1931 chromaticity diagram.

- Only applicable for sources close to the black body curve (white light).

- Standard source:
D_{65} (daylight, 6500 K) (x,y) = (0.312, 0.329)
E = Equal Energy point: (0.333, 0.333)

McCamy's approximate formula

$T_{CCT}=437n^3+3601n^2+6861n+5517$

where n=(x-0.3320)/(0.1858-y), and x, y are the CIE 1931 chromaticity coordinates.

Ref. McCamy, Color Res. Appl. **18**, 150 (1993).

Color Rendering Index (CRI)

- **Color Rendering Index (CRI)**: a numerical system that rates the "color rendering" ability of the light source in comparison with natural daylight (CRI=100, the highest possible CRI.).
- CRI is a relative measure of the colorimetric shift of an object when lit by a particular light source, compared with how the object would appear under a reference light source of similar color temperature.

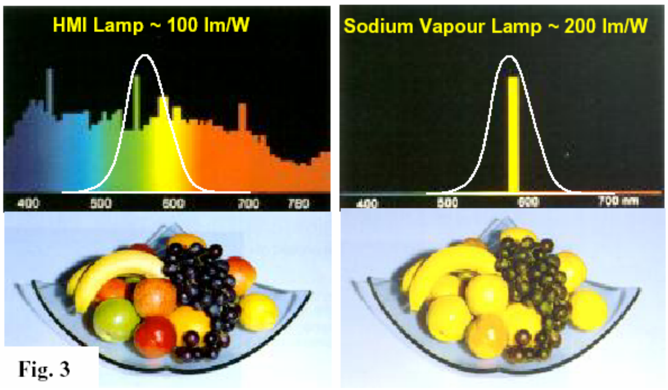


Fig. 3

Calculation Method of CRI

1. Select a reference illuminant
   (Planck blackbody radiation below 6000K)

$$S_r(\lambda) \xrightarrow{\bar{x},\bar{y},\bar{z}} x_r(\lambda),\ y_r(\lambda)$$

$$X = K\int_{380}^{780} S(\lambda)\bar{x}d\lambda \quad Y = K\int_{380}^{780} S(\lambda)\bar{y}d\lambda$$

$$Z = K\int_{380}^{780} S(\lambda)\bar{y}d\lambda$$

$$x = \frac{X}{X+Y+Z},\ y = \frac{Y}{X+Y+Z}$$

2. Measure the spectrum of the test source.

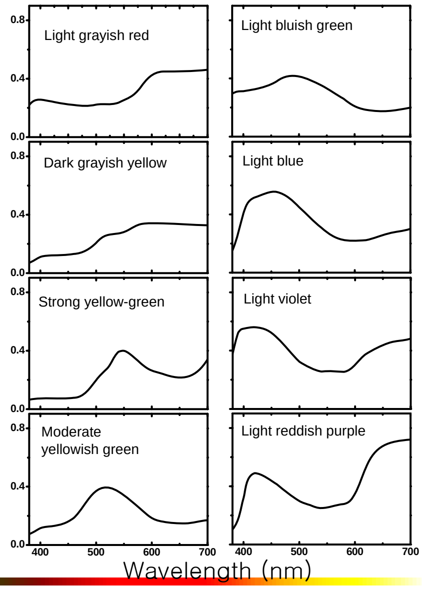
$$S_k(\lambda) \xrightarrow{\bar{x},\bar{y},\bar{z}} x_k(\lambda),\ y_k(\lambda)$$

3. Determine the reflected spectra from each of the eight test samples

$$S_r(\lambda)\rho(\lambda)_i \rightarrow (x_{ri}, y_{ri})$$

$$S_k(\lambda)\rho(\lambda)_i \rightarrow (x_{ki}, y_{ki})$$

Reflectivity spectra of eight test samples (CIE 1964)



Calculation Method of CRI

4. Transform the colorimetric data from the CIE 1931 values (X, Y, Z, *x, y*) to the (*u, v*) coordinates of the CIE 1960 *uniform chromaticity scale* (UCS) diagram by means of the following:

$$u = \frac{4X}{X + 15Y + 3Z} = \frac{4x}{-2x + 12y + 3}$$

$$v = \frac{6Y}{X + 15Y + 3Z} = \frac{6y}{-2x + 12y + 3}$$

5. To account for the adaptive color shift due to the different state of chromatic adaptation under the lamp to be tested and under the reference illuminant use the following formula:

$$u'_{ki} = \frac{10.872 + 0.404 c_r c_{ki} / c_k - 4 d_r d_{ki} / d_k}{16.518 + 1.481 c_r c_{ki} / c_k - d_r d_{ki} / d_k}$$

$$v'_{ki} = \frac{5.520}{16.518 + 1.481 c_r c_{ki} / c_k - d_r d_{ki} / d_k}$$

$$c = (4 - u - 10v) / v, \quad d = (1.708v + 0.404 - 1.481u)/v$$

Calculation Method of CRI

5. Calculate lightness indices for all reflected spectra:

$$W = 24Y^{1/3} - 17$$

6. Calculate the special color rendering indices for each test-color sample.

$$R_i = 100 - 4.6\{[W_{ki} - W_{ri}]^2 + 13^2[W_{ki}(u'_{ki} - u_r) - W_{ri}(u_{ri} - u_r)]^2 + 13^2[W_{ki}(v'_{ki} - v_r) - W_{ri}(v_{ri} - v_r)]^2\}^{1/2}$$

7. Calculate the general color rendering index.

$$CRI \text{ value}: \; R_a = \frac{1}{8}\sum_{i=1}^{8} R_i$$