Organic Light Emitting Diodes

有機發光二極體

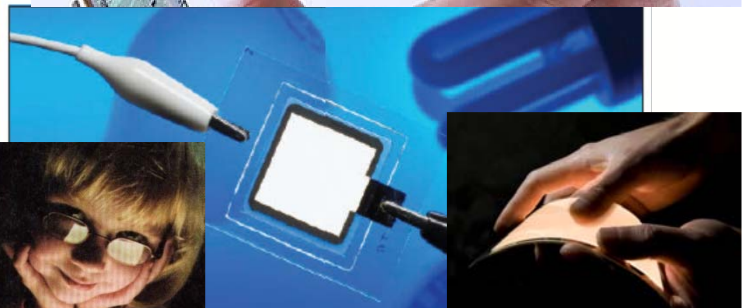
Smart phone

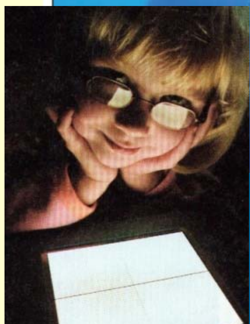
Samsung Galaxy S6 | Samsung Galaxy S6 Edge

Flexible displays!!

A curved TV

Ultrathin





Transparent

Flat and curved

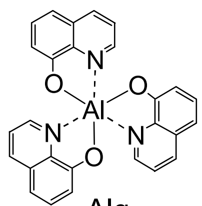
White OLED for solid state lighting

The Evolution of OLEDs

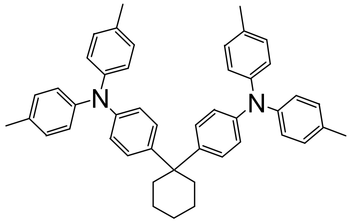
1. Multilayer OLEDs structure requires nanometer thickness to work!
2. A good interfacial energy alignment is necessary to reduce driving voltage

現在

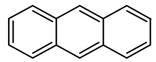
Present



Alq3 (600 Å)



Diamine (750 Å)

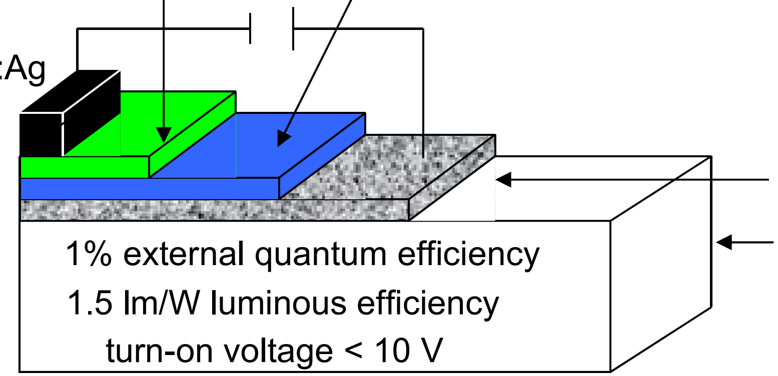


anthracene crystal (10~20 μm)

過去

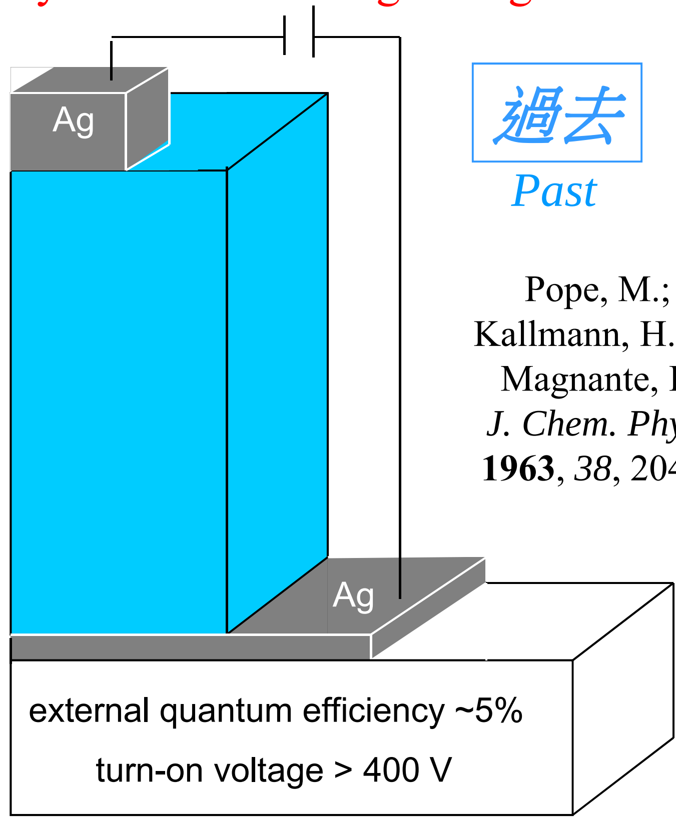
Past

Pope, M.; Kallmann, H. P.; Magnante, P. *J. Chem. Phys.* **1963**, *38*, 2042.

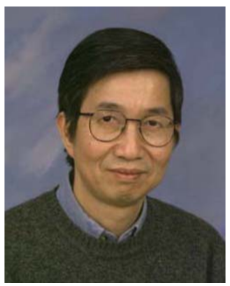


ITO

Glass



Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.



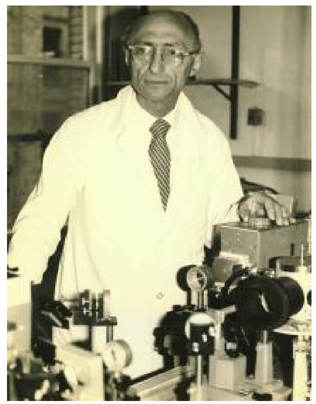
Dr. Ching W. Tang
（鄧青雲 博士）

Eastman Kodak Company

Now at University of Rochester

Prof. Martin Pope

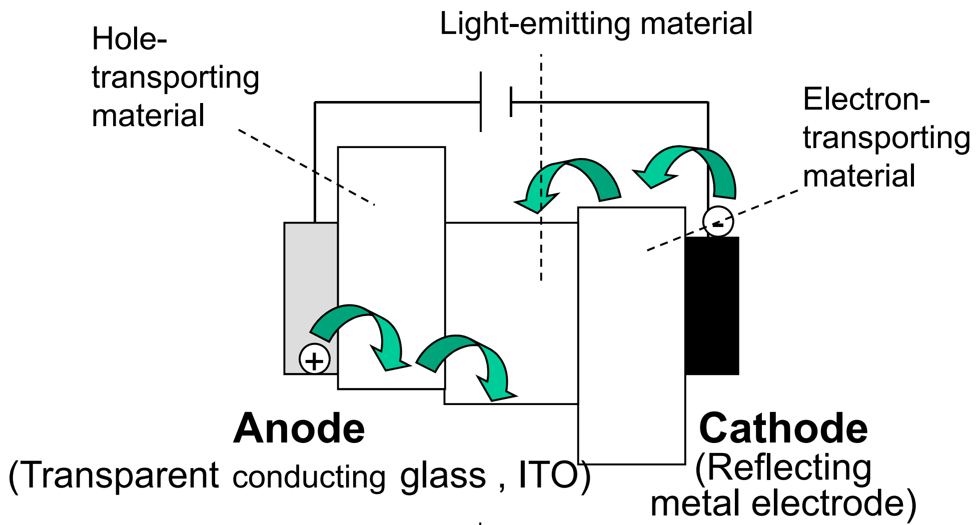
Professor emeritus
New York University



Structure of OLED and the Origin of Electroluminescence

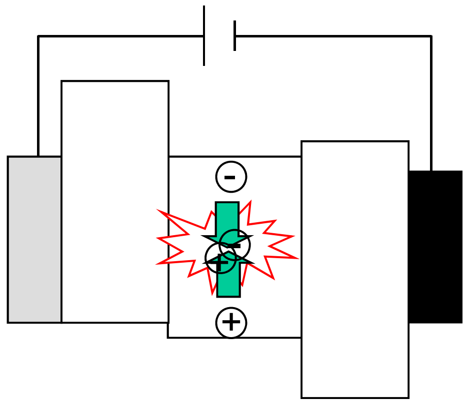
1. Hole and electron injection

2. Hole and electron transportation

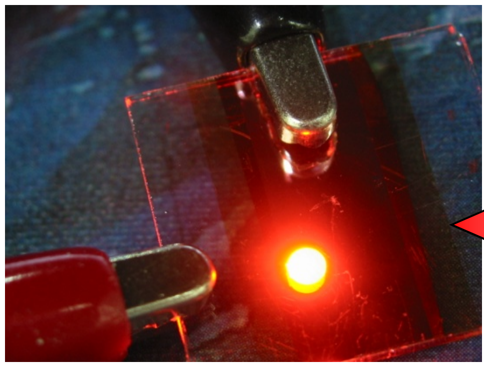


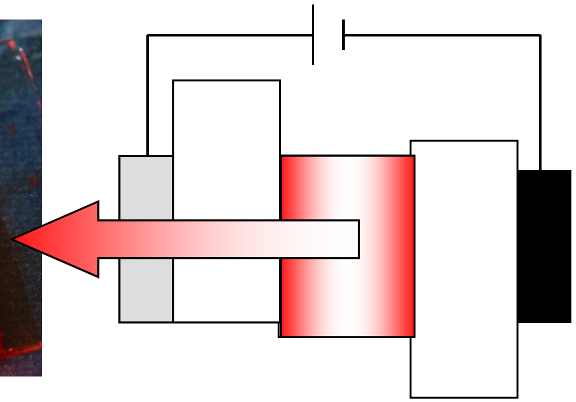
3. Hole and electron recombination
   and exciton formation

4. Exciton to photon (electroluminescence)



5. Light out put from OLED

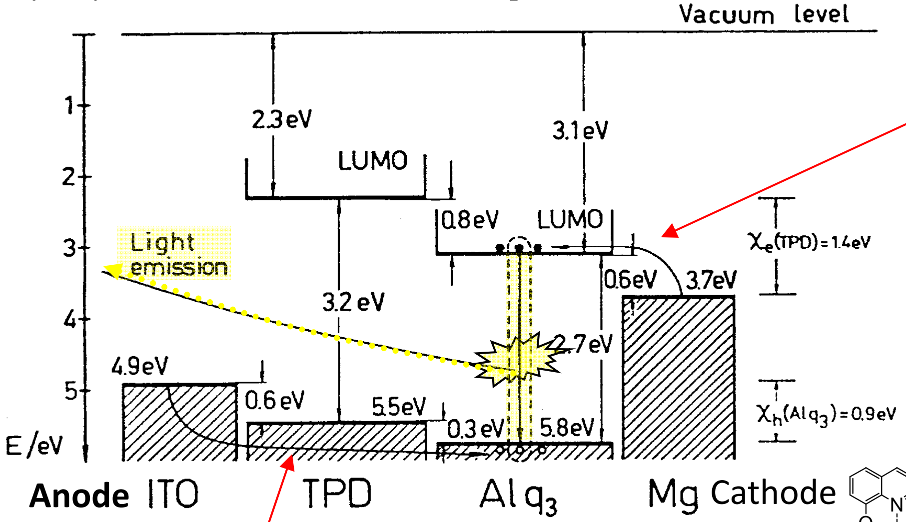


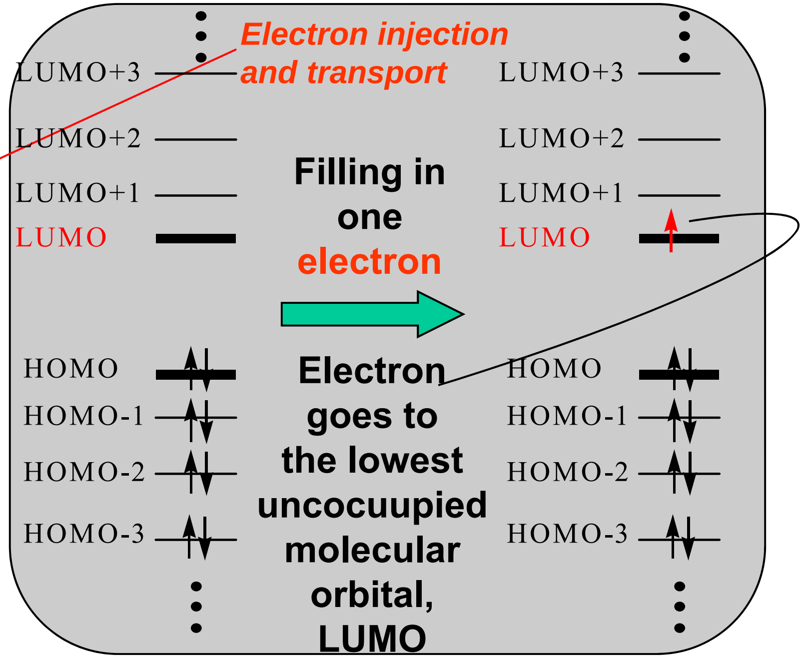


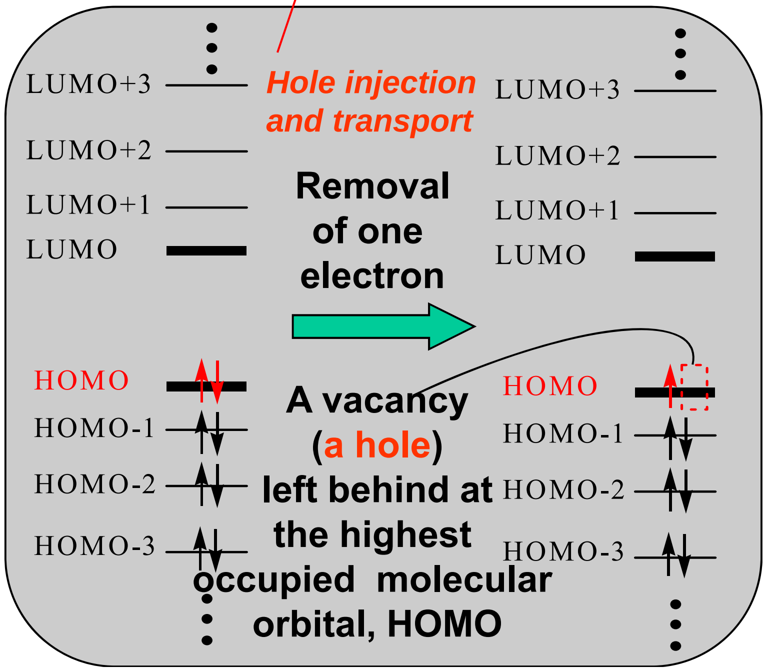
Charge-Injection and Charge-Transport in OLEDs

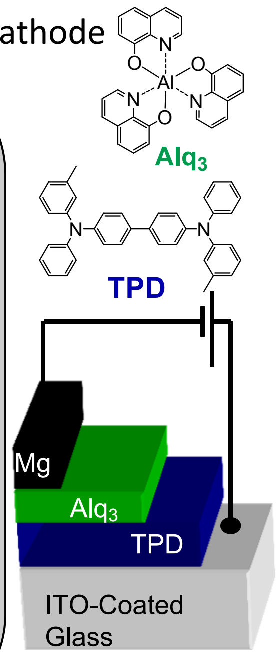
Alignment of energy levels among electrodes and organic materials

Kalinowski, J. in *Organic Electroluminescent Materials and Devices* edited by Miyata, S. and Nalwa, H. S., 1997, p. 52.

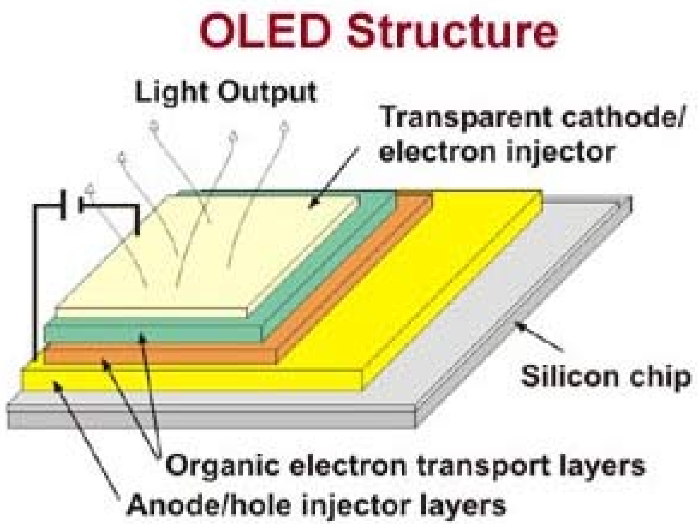




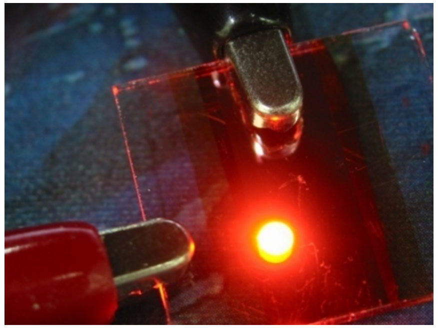


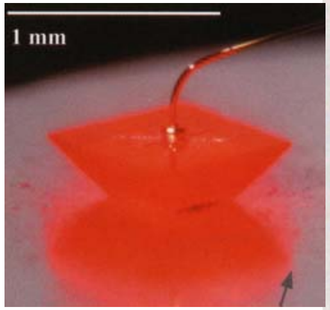


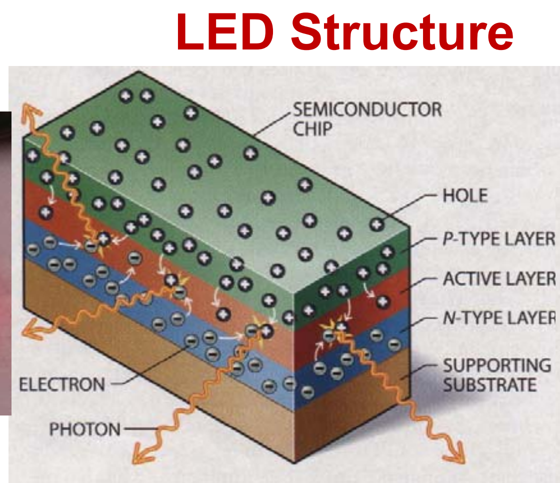
Element	Work Function (eV)	Element	Work Function (eV)
Cs	2.14	Ag	4.26
K	2.30	Al	4.28
Ba	2.70	Nb	4.30
Na	2.75	Cr	4.50
Ca	2.87	Cu	4.65
Li	2.90	Si	4.85
Mg	3.66	Au	5.10
In	4.12		

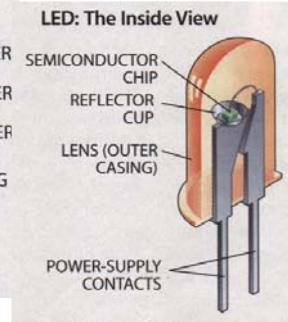


多層薄膜狀態，每層厚度不到 0.0001公分 Multilayer thin-film structure of which thickness is less than 1 μm







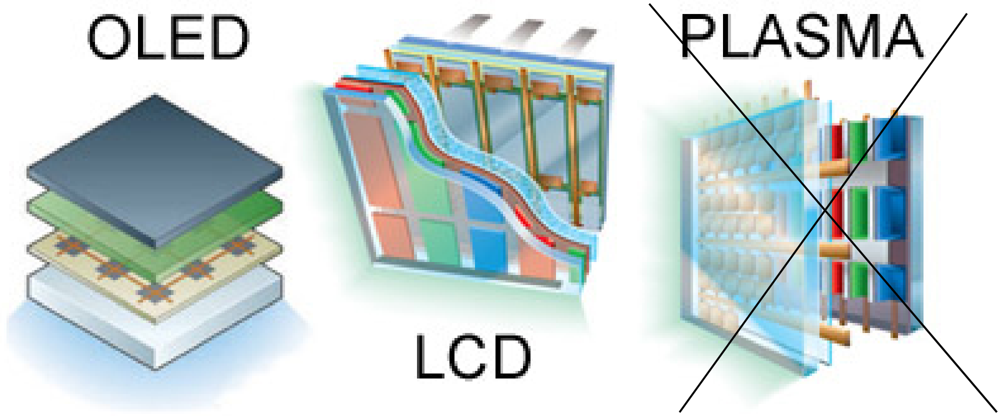


塊狀或顆粒狀態磊晶，
厚度至少為0.1公分，且非連續性薄膜。A microscopic layer of crystalline block materials (thickness greater than 0.1 cm) grown by epitaxial doping process

OLED display can be flexible

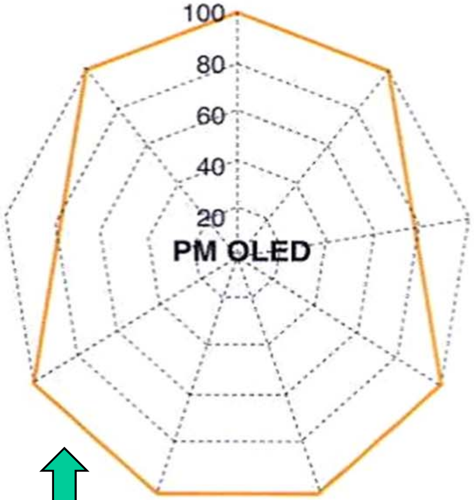
三種最常見到的平面顯示器技術

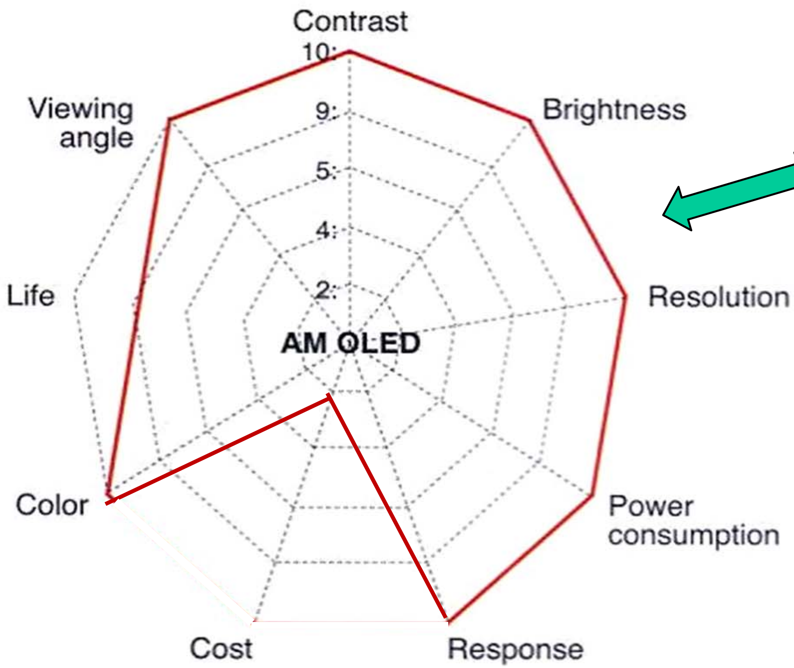
Common Flat Panel Display Technologies

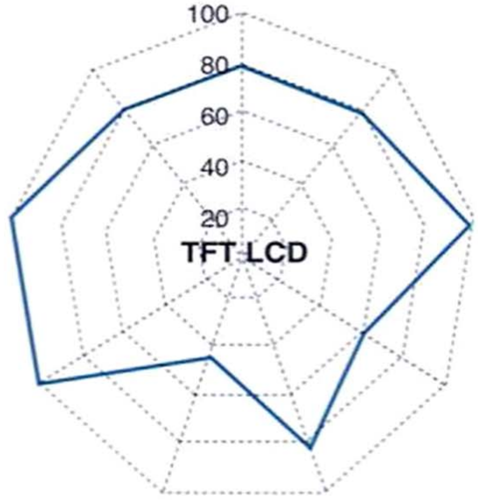


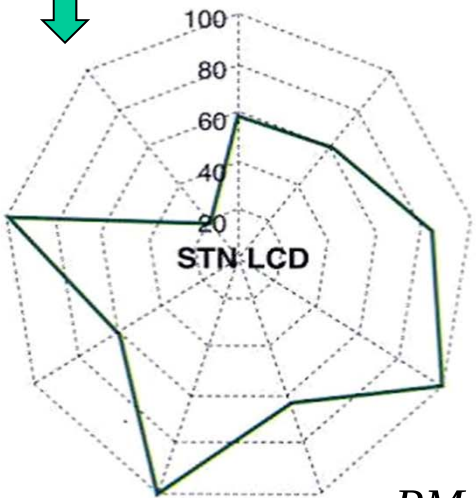
不同驅動法之LCD與OLED之比較

Comparison of LCD and OLED with different driving method



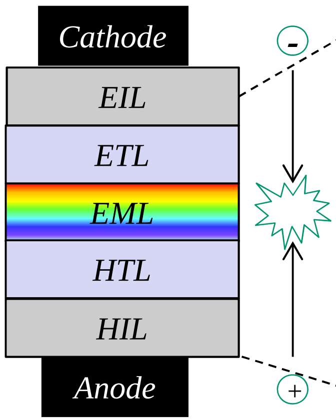






PM OLED: Passive matrix-driven OLED *主動列陣(矩陣)驅動OLED*

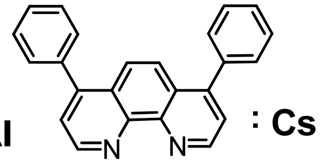
AM OLED: Active matrix-driven OLED *被動列陣(矩陣)驅動OLED*



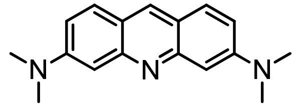
Electron Injection Materials

LiF/Al

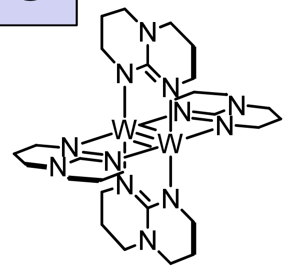
CsF/Al



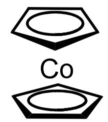
BPhen (*n*-dopant)



AOB (*n*-dopant)



$W_2(hpp)_4$ (*n*-dopant)



Cp_2Co (*n*-dopant)

novaled

Novaled AG Dresden Co

US Patent 7919010 B2 2011

US Patent 8258501 B2 2012

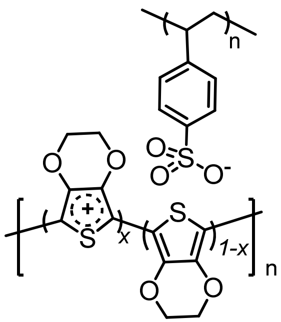
US Patent 2012/0217483 A1

Dopant materials *NDP-Series*

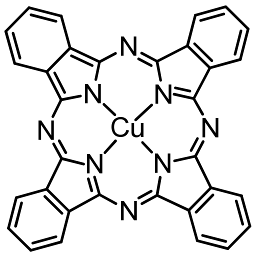
NDN-Series

Hole Injection Materials

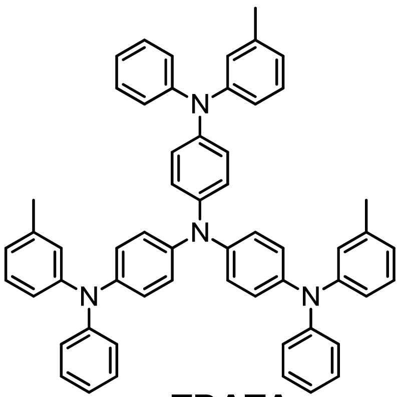
PEDOT:PSS, CuPc, mTDATA, CF_x, MoO_3, MeO-TPD:F_4-TCNQ



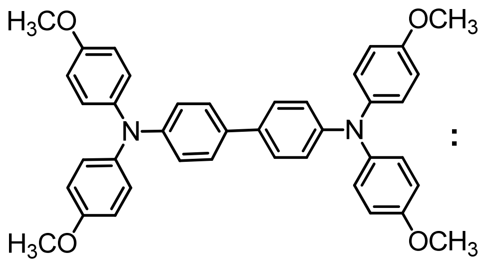
PEDOT:PSS



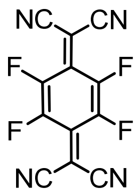
CuPc



***m*TDATA**



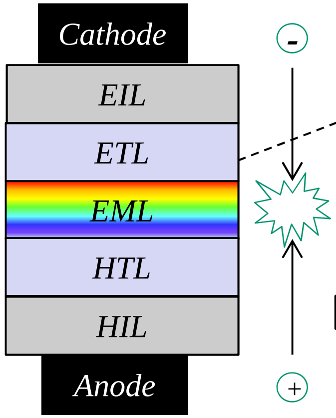
MeO-TPD



F_4-TCNQ (*p*-dopant)

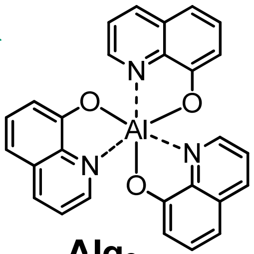
Electrode work function matching *Ohmic contact* *Interlayer*

形成與金屬或金屬氧化物電極、功函數匹配、歐姆接觸、均勻中間層

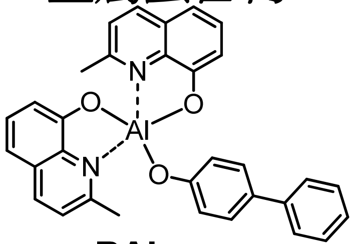


Electron Transporting Materials

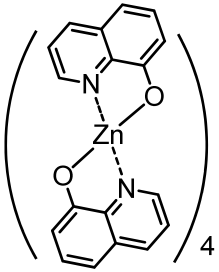
Metal chelates 金屬螯合物



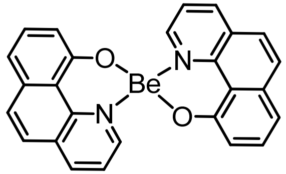
Alq_3



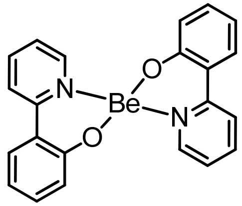
BAlq



Znq_2



Bebp2



Bepp2

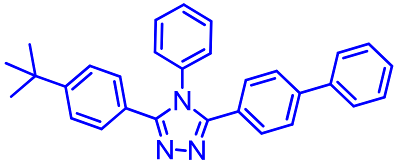
μ_e = 1.4 x 10^{-6} cm^2/Vs
HOMO = ~5.9 eV
LUMO = ~3.3 eV

Hole blocking Materials

With deep HOMO energy level
很深的HOMO能階

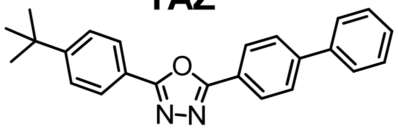
Aza-containing heterocyclic 含氮雜環

⇨ ***Electron deficient 缺電子性的***



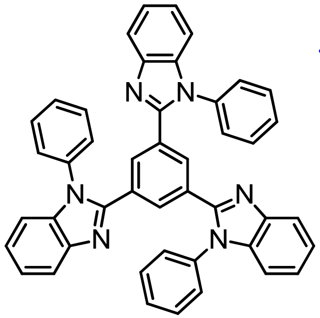
TAZ

μ_e = 1 x 10^{-6} cm^2/Vs
HOMO = 6.6 eV
LUMO = 2.6 eV



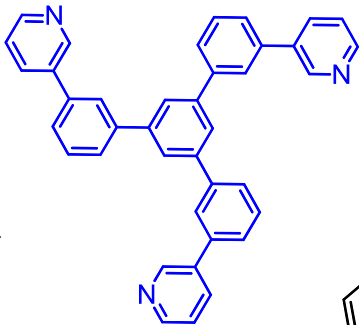
PBD

μ_e = 1.9 x 10^{-5} cm^2/Vs
HOMO = 6.3 eV
LUMO = 3.0 eV



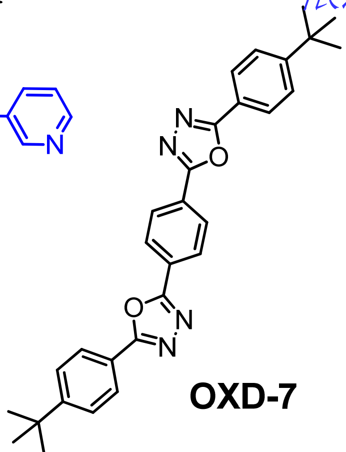
TPBI

μ_e = 3-8 x 10^{-5} cm^2/Vs
HOMO = 6.2 eV
LUMO = 2.7 eV



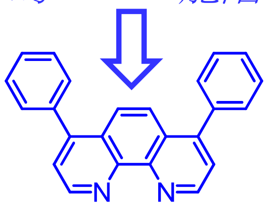
T*m*PyPB

μ_e = 5 x 10^{-4} cm^2/Vs
HOMO = 6.7 eV
LUMO = 2.6 eV

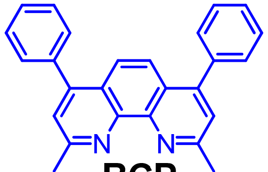


OXD-7

μ_e = 2.1 x 10^{-5} cm^2/Vs
HOMO = 6.3 eV
LUMO = 3.0 eV



BPhen

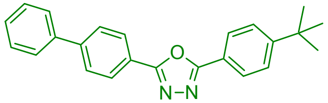


BCP

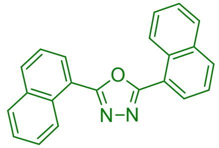
μ_e = 4 x 10^{-4} cm^2/Vs
μ_e = 1 x 10^{-3} cm^2/Vs
HOMO > 6.4-6.5 eV
LUMO > 2.9-3.0 eV

Heterocyclic Compounds as Electron-Transporting and/or Light Emitting Materials

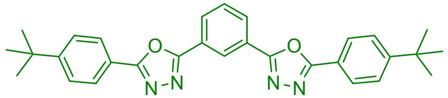
Oxadiazole



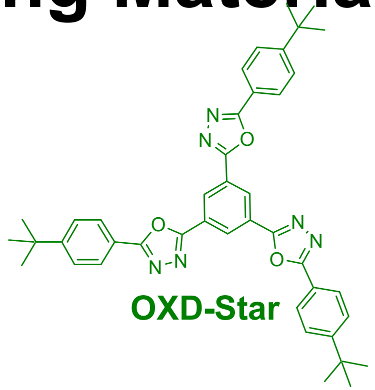
PBD



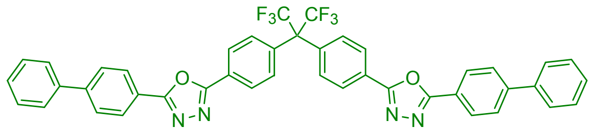
BND

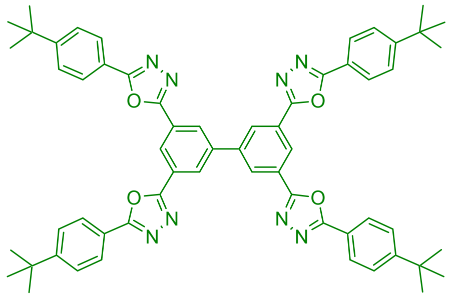


OXD-7

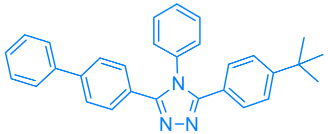


OXD-Star

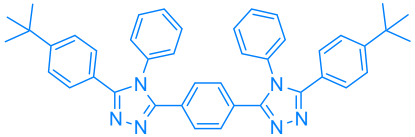




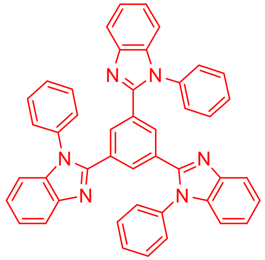
Triazole



TAZ

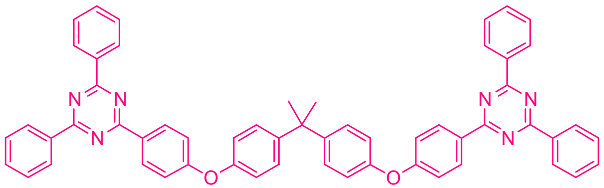


Phenylbenzimidazole

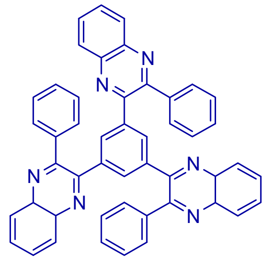


TPBI

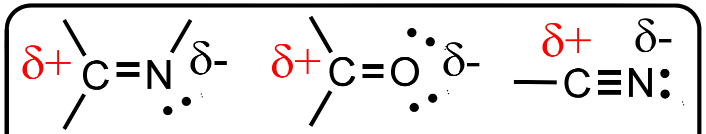
Triazine



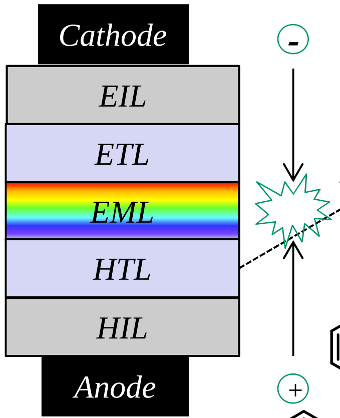
Phenylquinoxaline



Those nitrogen-containing heterocyclic aromatics (electron poor or deficient) having low energy level of LOMO are readily to be reduced and hence suitable for electron transport



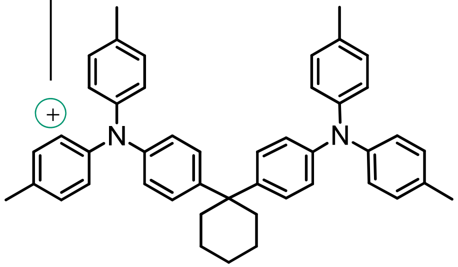
Electron deficient center (δ+)
facilitating electron transport



Hole Transporting Materials

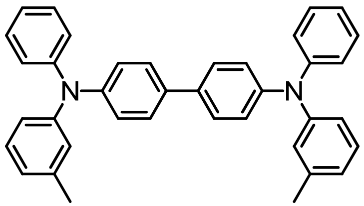
Triarylamine *are readily to be oxidized and hence low lying HOMO energy level*

⇨ ***Electron rich 富有電子性的***



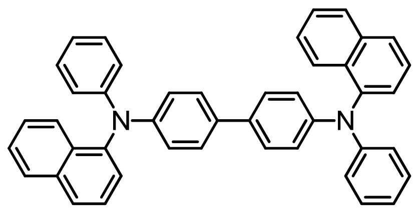
TAPC

μ_h = 1 x 10^{-2} cm^2/Vs
HOMO = 5.8 eV
T_g = ~78 °C



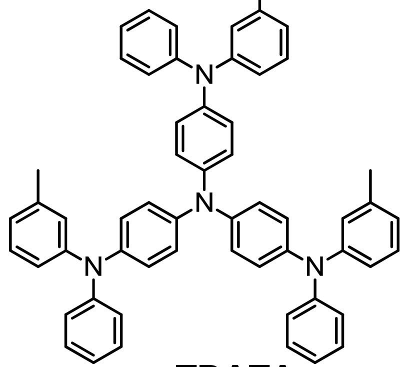
TPD

μ_h = 1 x 10^{-3} cm^2/Vs
HOMO = 5.4 eV
T_g = ~60 °C



NPB (α-NPD)

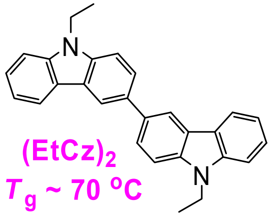
μ_h = 5.1 x 10^{-4} cm^2/Vs
HOMO = 5.1 eV
T_g = ~95 °C



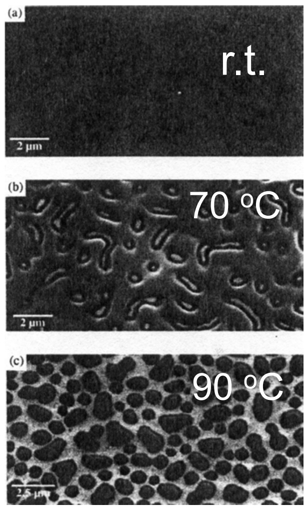
***m*TDATA**

μ_h = 3 x 10^{-5} cm^2/Vs
HOMO = 5.1 eV
T_g = ~75 °C

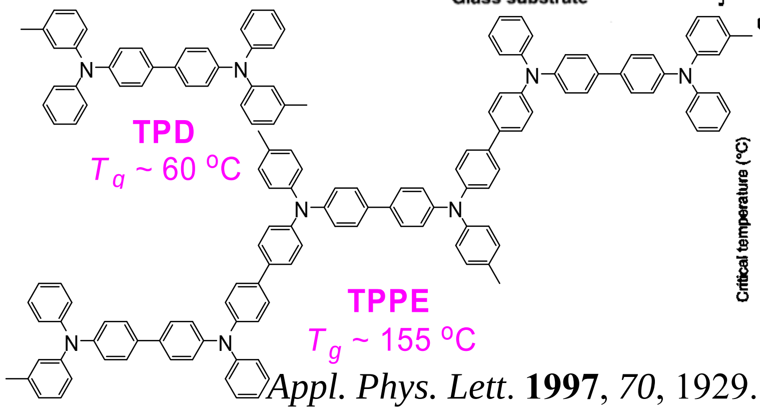
Morphological stability (and device stability) of amorphous thin films



$(EtCz)_2$
T_g ~ 70 °C



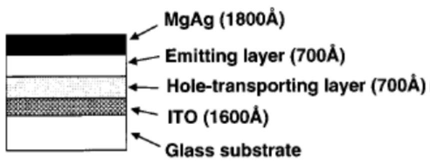
Adv. Mater. **1999**, *11*, 112.

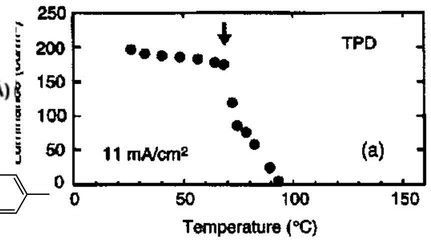


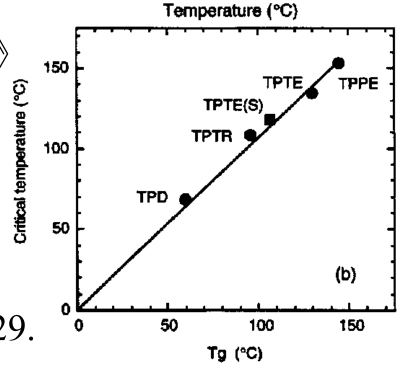
TPD
T_g ~ 60 °C

TPPE
T_g ~ 155 °C

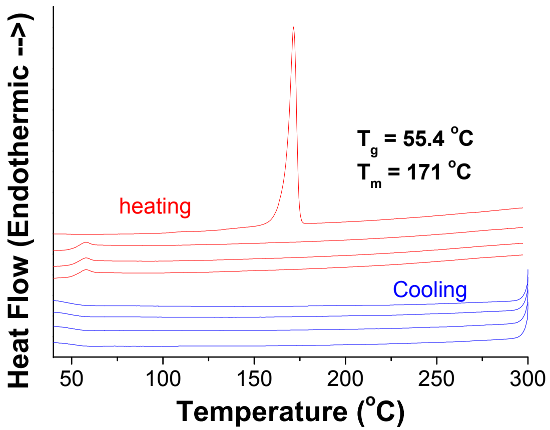
Appl. Phys. Lett. **1997**, *70*, 1929.

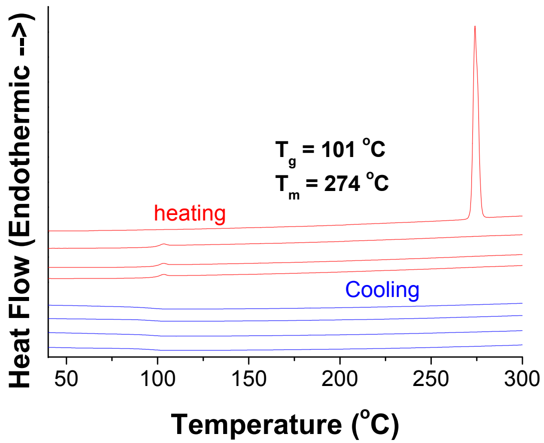


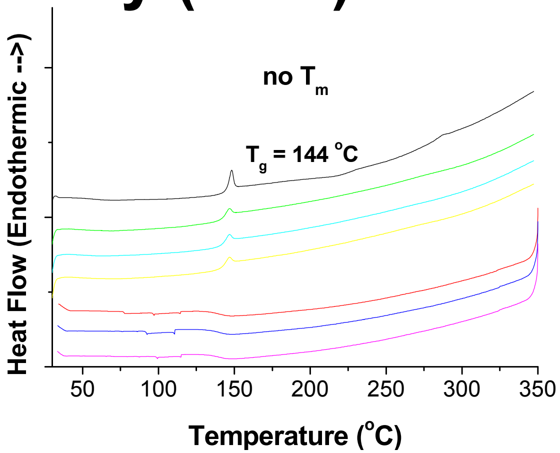




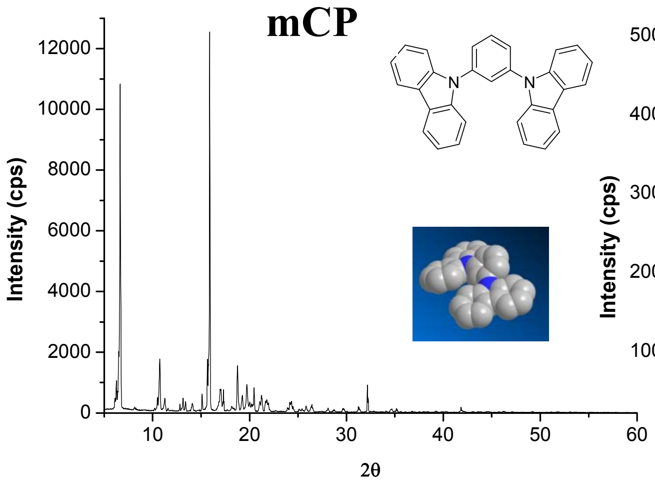
Differential Scanning Calorimetry (DSC)

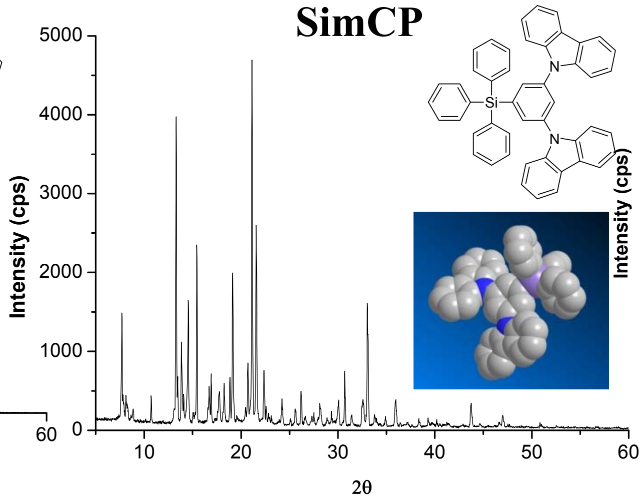


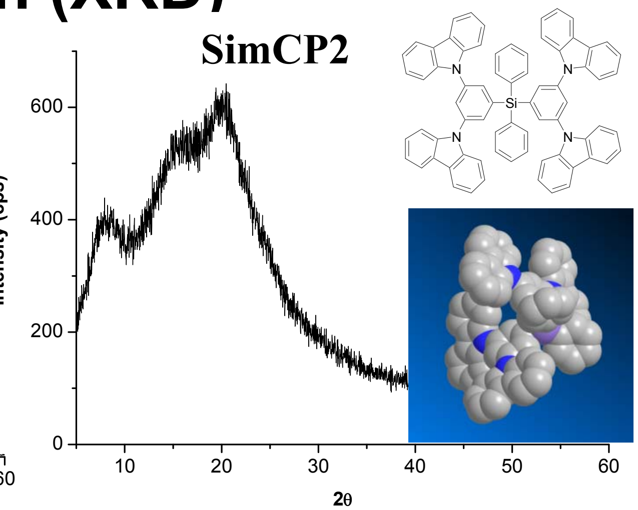




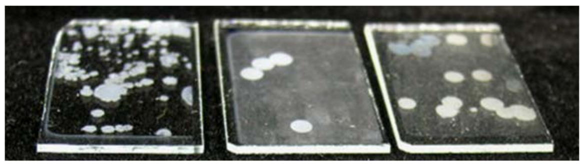
Powder X-Ray Diffraction (XRD)







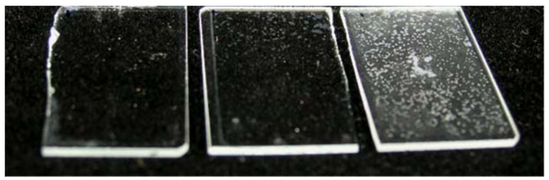
Crystallinic



Pristine 70 °C 120 °C

T_g ~ 60 °C

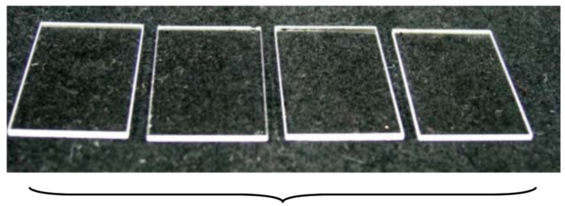
Crystallinic



Pristine 70 °C 120 °C

T_g ~ 110 °C

Truly Amorphous



150 °C (T_g ~ 150 °C)

Issues Important for OLEDs

- **Reliability (operation lifetime) 壽命**

  10000 (polymeric film) ~ 100000 (molecular film) hours @ 200 cdm^{-2}

  Encapsulation problems:

  H_2O and O_2 from air damage OLED devices

  Electrode problems:

  Charge-injection interface barrier

  Diffusion and degradation of ITO anode and metal cathode)

  Material problems:

  Crystallization (Low T_g) of molecular materials

- **Color tuning of light-emitting materials 色彩**

  π-conjugation length and donor-acceptor approaches

  Red (R), green (G), and blue (B) for full color displays

  B + yellow (or orange) for two color white OLED lighting

  B + G + R for three color white OLED lighting

- **Efficiency (photon/electron) 效率**

  <5% (*fluorescence-based*) compared to >10% of commercial light bulbs

  Phosphorescence materials are necessary particularly in the white OLED lighting application

Units of OLED Efficiency

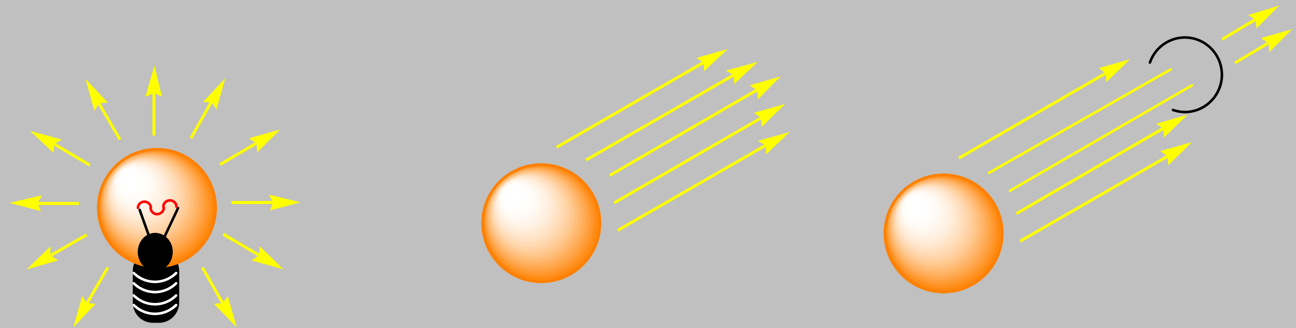
- **External Quantum Efficiency (%)**
  = (Photon# / Electron#) • 100%

- **Luminance Efficiency (cd/A)**
  (Photometric Efficiency, Current Efficiency)

Luminance (L) : cd/m^2
Current density (J) : mA/cm^2
Current (I): Amp (A)
Watt (W): W = I •V
lm = π •cd

- **Power Efficiency (lm/W)**

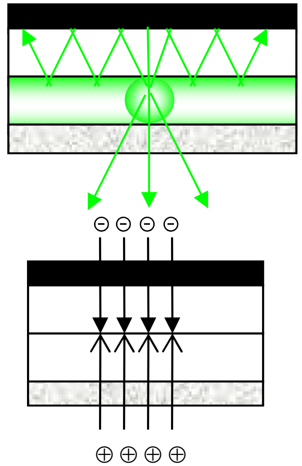
$$lm/W = (\pi \bullet cd)/(I \bullet V) = \pi/V \bullet cd/I$$
$$= \pi/V \bullet cd/(J \bullet cm^2 \bullet 1000)$$
$$= \pi/V \bullet cd/(J \bullet m^2/ 10000 \bullet 1000) = \pi/V \bullet cd/(J \bullet m^2/ 10)$$
$$= \pi/V \bullet 10/J \bullet cd/ m^2 = (10\ \pi)/(VJ) \bullet L$$



Name:	Luminous flux	Luminous Intensity	Luminance
Unit:	Lumen (lm)	Candela (cd)	$Candela/m^2$ (nit) (L)

Theoretical External Quantum Efficiency (η_{EXT} or EQE) of OLEDs

$$\eta_{EXT} = \alpha \cdot \gamma \cdot \eta_r \cdot \psi_{pl}$$



α : Light output coupling factor $\alpha = 1/(2n^2) \approx 20\%$

n: refractive index of the emission medium

($n = 1.7$ in Alq_3-based devices)

γ : Probability of carrier recombination (charge balance factor)

maximum $\gamma \sim 100\%$

η_r : Production efficiency of an exciton

25% for singlet-state (fluorescence)

75% for triplet-state (phosphorescence)

75% *triplete state* → $\alpha(1)\alpha(2)$; $\beta(1)\beta(2)$; $\sigma_+ = \alpha(1)\beta(2) + \alpha(2)\beta(1)$

25% *singlete state* → $\sigma_- = \alpha(1)\beta(2) - \alpha(2)\beta(1)$

Triplet state: symmetry is not changed by exchange spin label
Singlet sate: symmetry is changed by exchange spin label

φ_{pl}: Fluorescence or phosphorescence (photoluminescence, PL) quantum yields

50% ~100% for most organic compounds

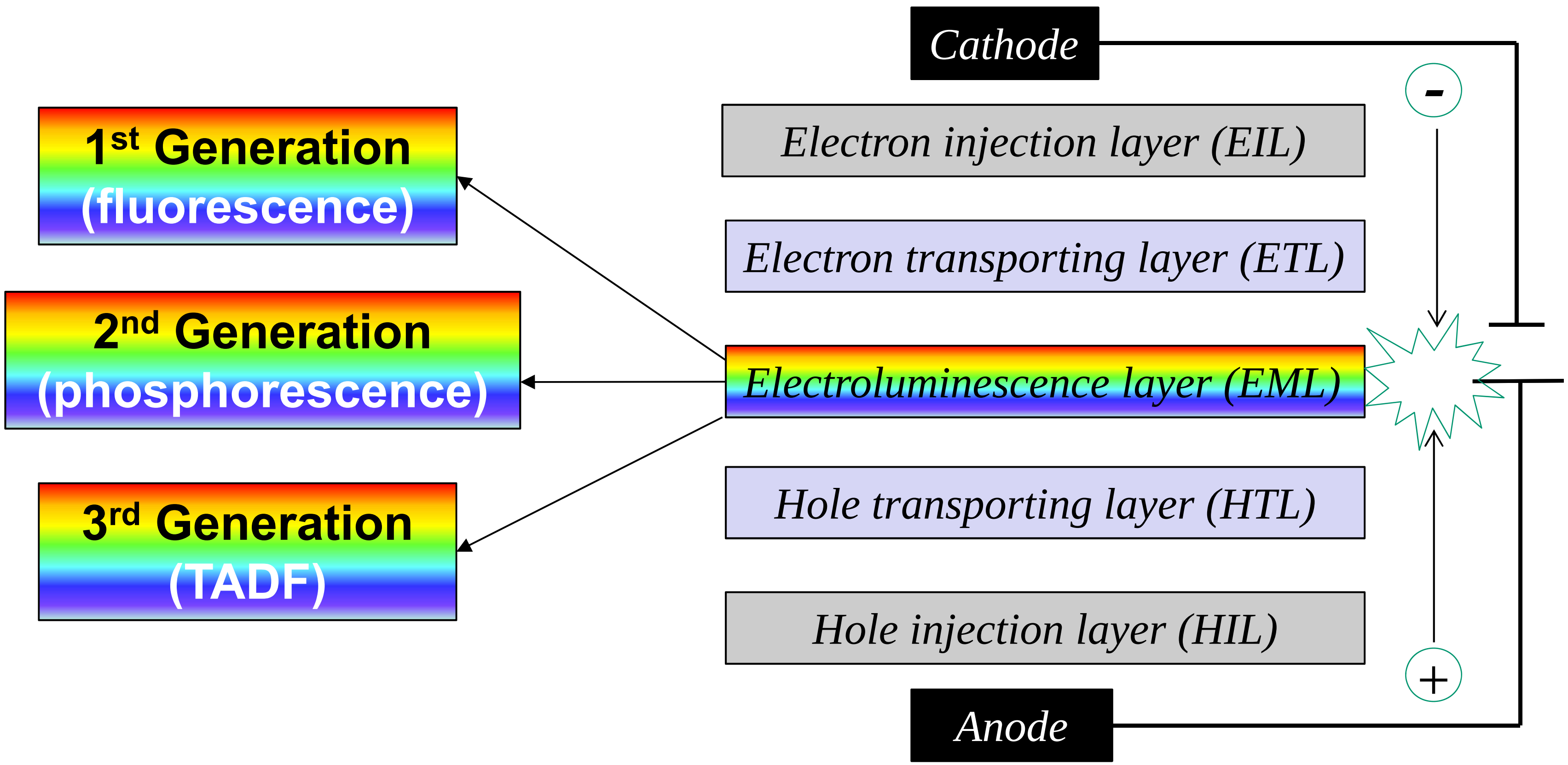
T. Tsutsui, *MRS Bull*. **1997**, *22(6)*, 39.

Maximum η_{EXT} is

2.5%~5% for fluorescent materials

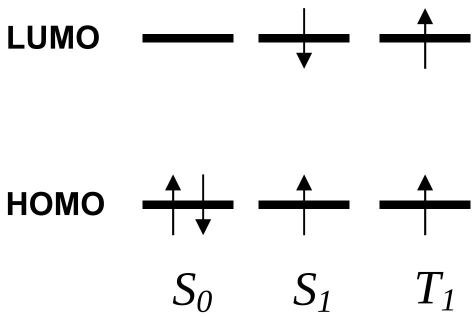
7.5%~15% for phosphorescent materials

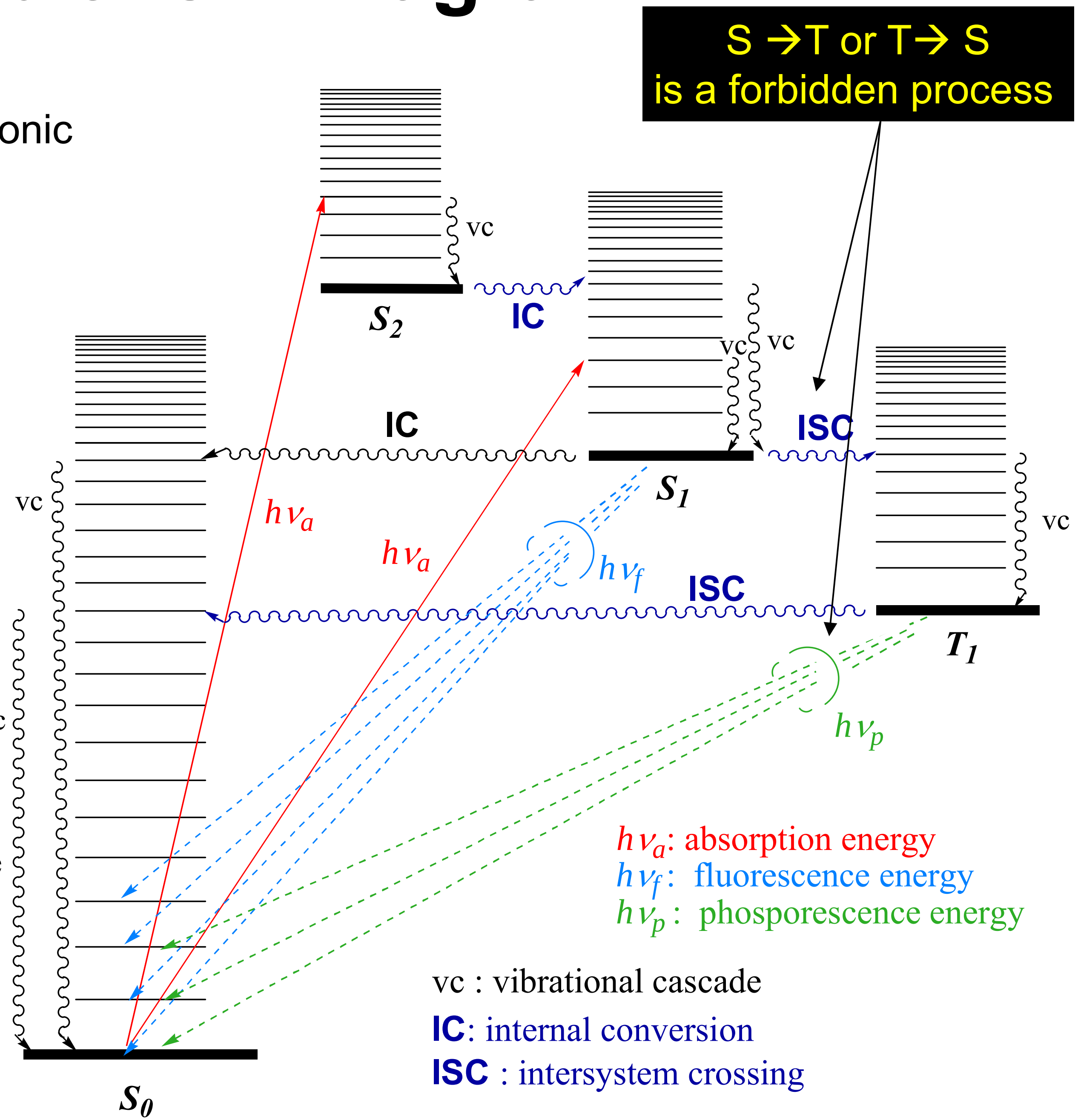
Light-Emitting Materials of OLED



Jablonski Diagram

Illustration of possible electronic process following photon absorption with energy $h\nu_a$





S_0: singlet ground state

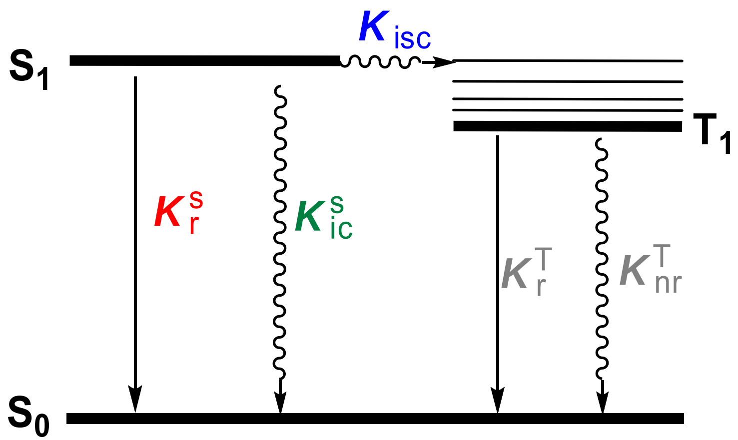
S_2: second lowest singlet excited state

S_1: lowest singlet excited state

T_1: lowest triplet excited state

Fluorescence Quantum Yield (Φ_F) and Fluorescence lifetime (τ_F)

Excited States



Ground State

***K* : rate constant**

Singlet (excited) state non-radiation decay rate constant

$$K_{nr}^{s} = K_{ic}^{s} + K_{isc}$$

K_r^S, K_r^T : radiation decay (emission) rate constants

Fluorescence lifetime ~ nanosecond 10^{-9} s

Phorescence lifetime > microsecond 10^{-6} s

Fluorescence quantum yield $\Phi_F = \dfrac{K_r^s}{K_r^s + K_{nr}^s} = K_r^s \tau_s$

Phosphorescence quantum yield $\Phi_P = \dfrac{K_r^T}{K_r^T + K_{nr}^T} = K_r^T \tau_T$

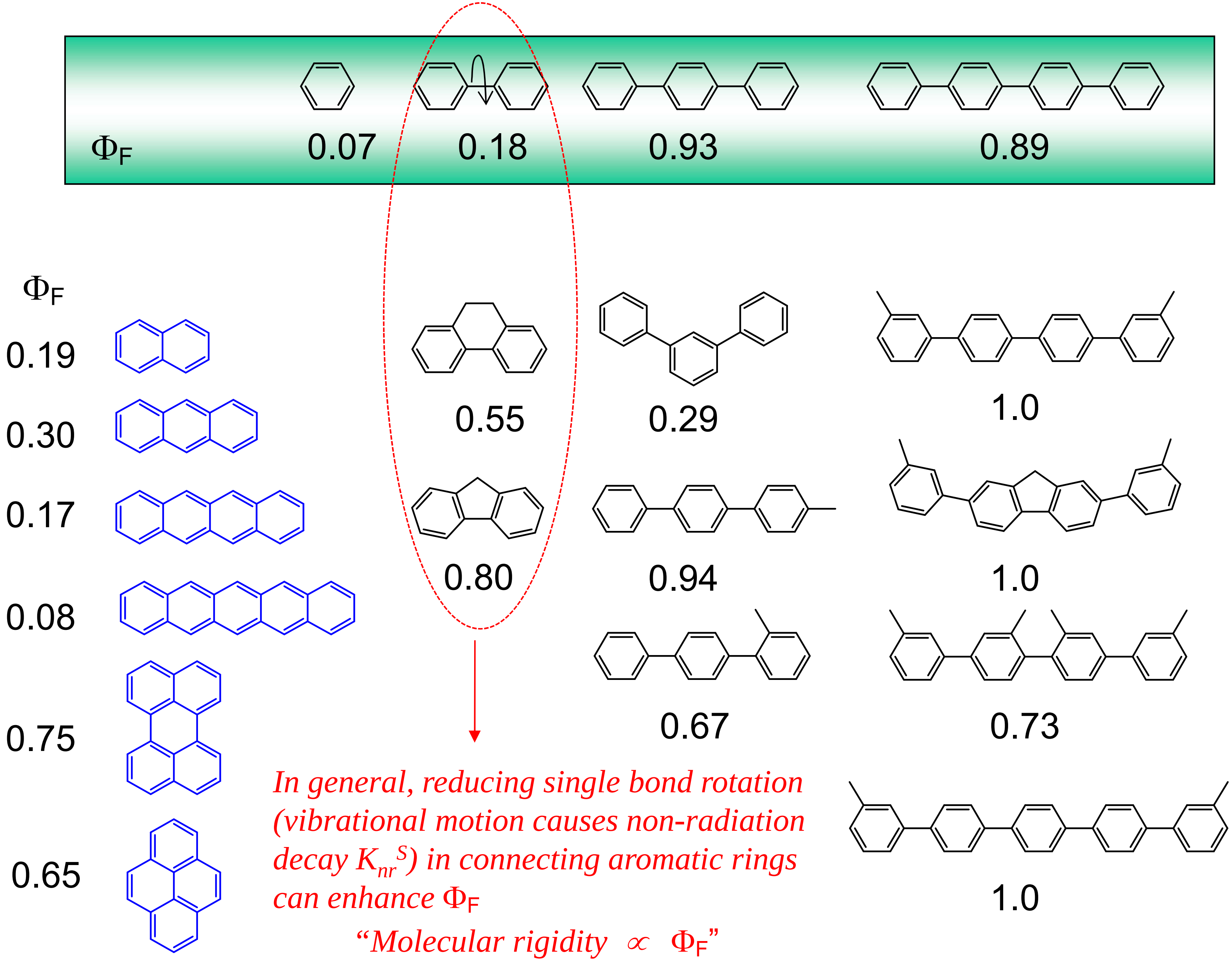
$\tau_s = \dfrac{1}{K_r^s + K_{nr}^s}$ (lifetime of excited state **S1**) ; $\tau_T = \dfrac{1}{K_r^T + K_{nr}^T}$ (lifetime of excited state **T1**)

For most organic species, K_{isc} is much smaller than K_{ic}^{s}. Therefore

$\tau_s \approx \dfrac{1}{K_r^s + K_{ic}^s}$ *and* $\Phi_F \approx \dfrac{K_r^s}{K_r^s + K_{ic}^s}$

Since Φ_F *and* τ_s are determined by experimental method, K_r^S and K_{ic}^S can be estimated by calculation (similarly for K_r^T and K_{nr}^T).

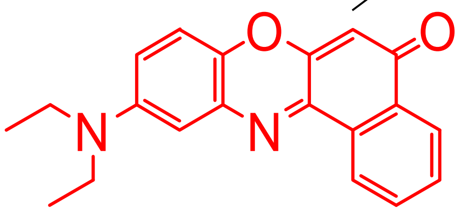
Molecular Structure and Fluorescence Quantum Yield Φ_F



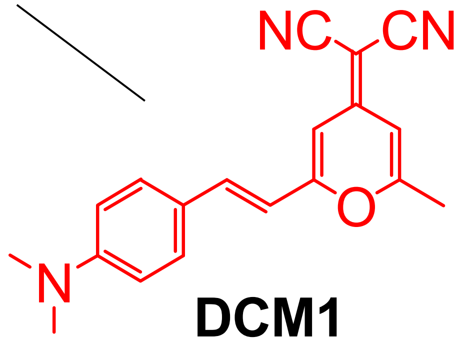
In general, reducing single bond rotation (vibrational motion causes non-radiation decay K_{nr}^{S}) in connecting aromatic rings can enhance Φ_F

"Molecular rigidity $\propto$ Φ_F"

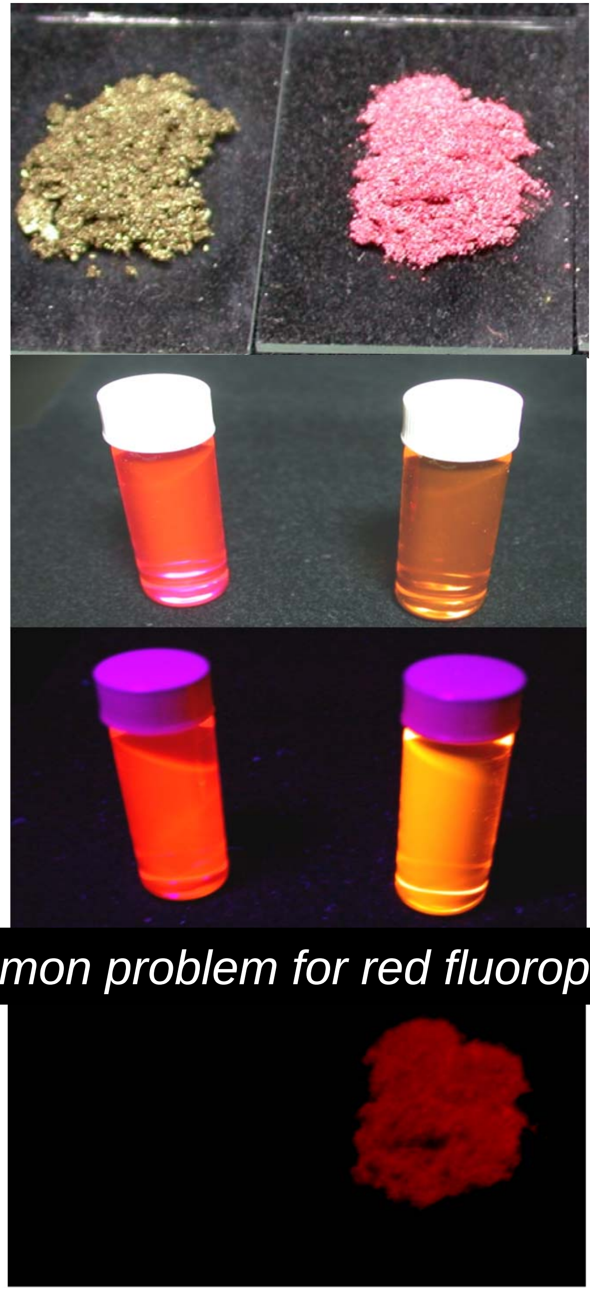
Fluorescence Quenching in Solid State



Nile Red



DCM1



ϕ_f ~70%

ϕ_f ~20%

-100%

-75%

A common problem for red fluorophores!!

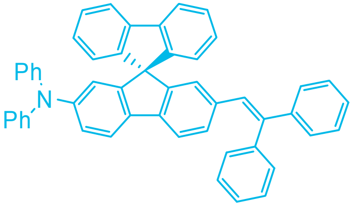
ϕ_f ~0%

ϕ_f ~5%

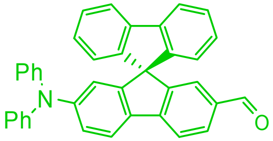
Chen, C.-T.

Chem. Mater. **2004**, *16*, 4389.

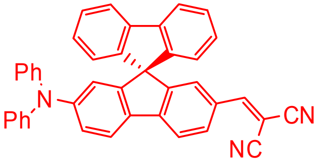
The Chemical Approach in Achieving Red Fluorescence



μ ~ 1 Debye
ϕ^{f}_{solid} ~ 51%



μ ~ 5 Debye
ϕ^{f}_{solid} ~ 42%



μ ~ 11 Debye
ϕ^{f}_{solid} ~ 33%

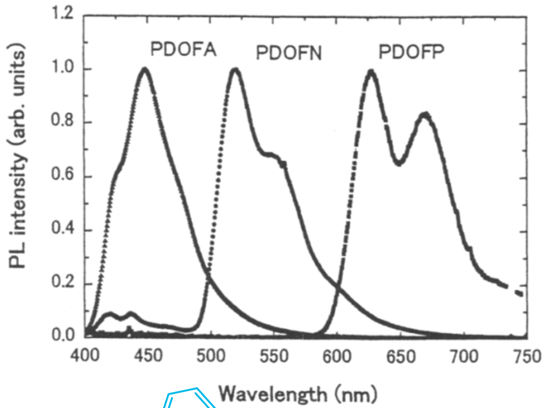
C. -T. Chen *et al*
Adv. Funct. Mater. **2008**, *18*, 248.

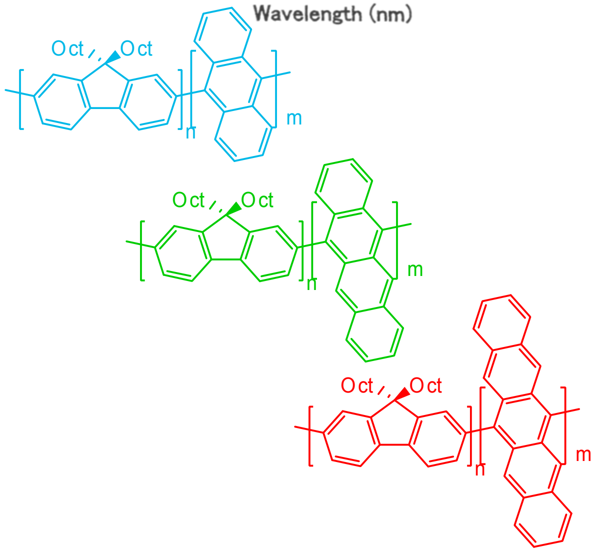
Red Fluorophores

Donor-acceptor-substituted π-conjugated molecules	Aromatic molecules with extended π-conjugation
Molecules with **large dipole moment**	Molecules with **flat planar shape**
Molecular aggregation due to dipole-dipole interaction	Molecular stacking due to π-π interaction

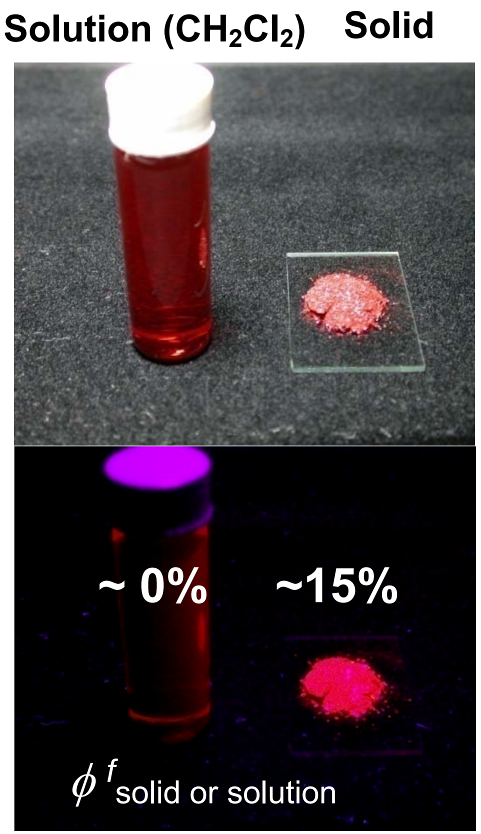
Solid state fluorescence quenching

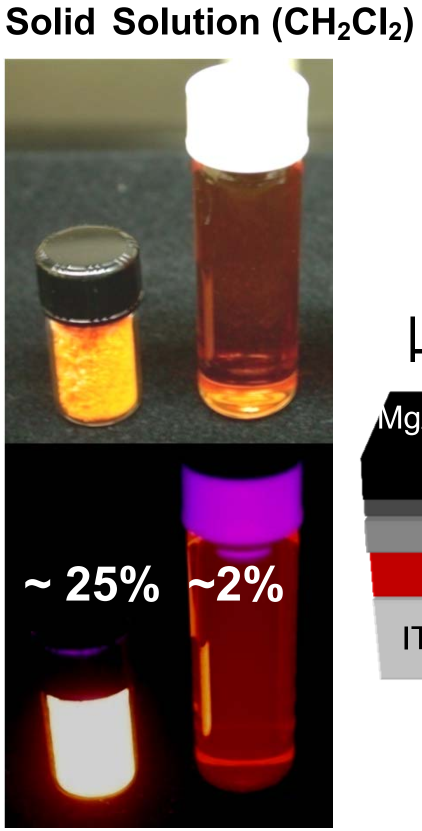
S. Tokito *et al Proc. SPIE*, **2001,** *4105*, 69.

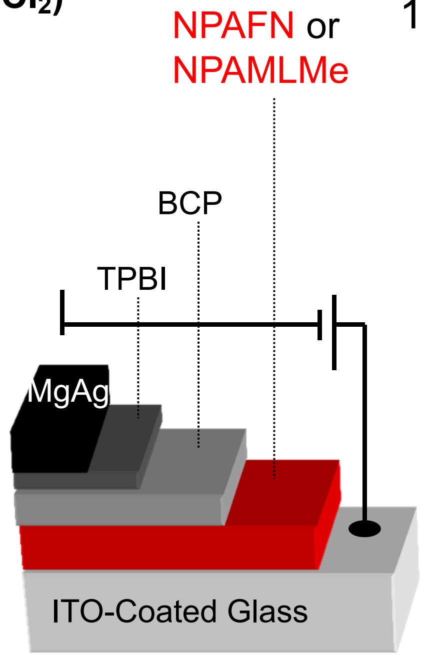


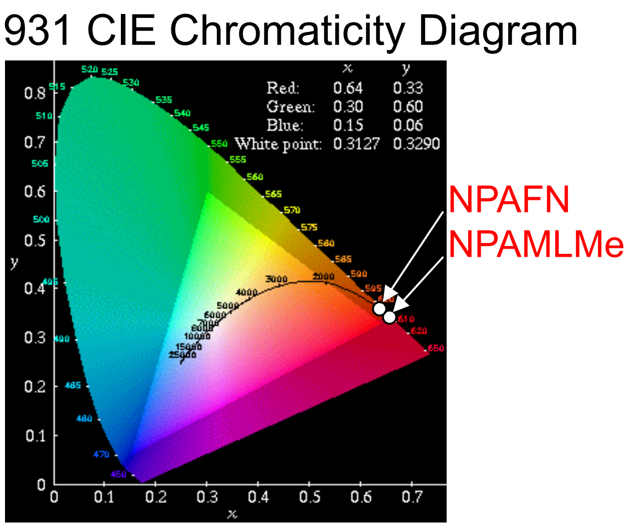


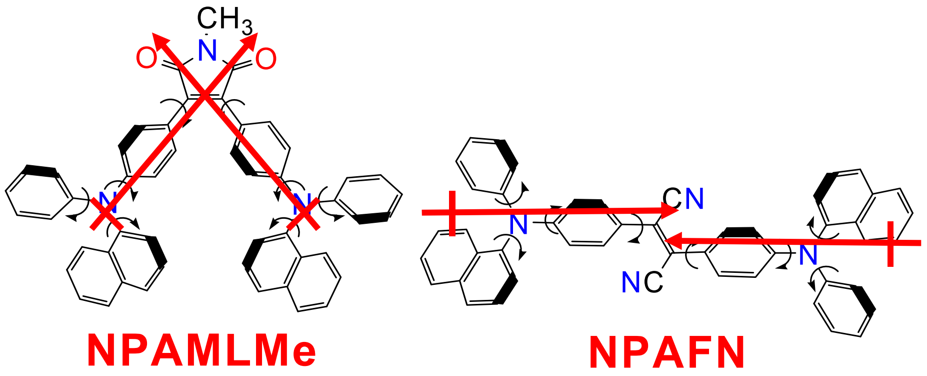
Fluorescence of Non-Dopant Red Fluorophores and OLEDs











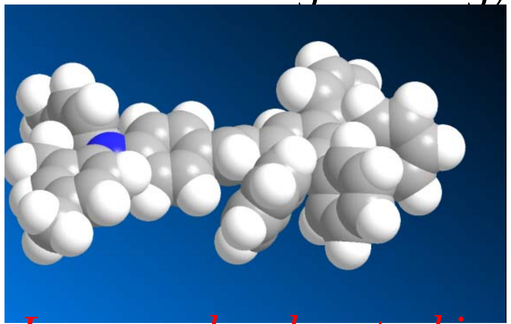
ITO/NPAMLMe or NPAFN/BCP/TPBI/Mg:Ag

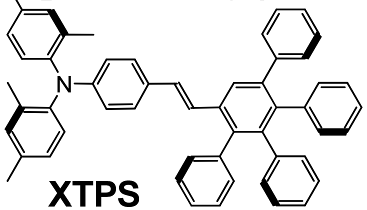
OLED performance	NPAMLMe	NPAFN
λ_{max}^{EL} (nm)	650	634
1931 CIE (*x*, *y*)	(0.66, 0.33)	(0.64, 0.33)
Maximum Efficiency (η_{EQE})	2.4%	2.4%
η_{EQE} @ 20 mA/cm^2	2.3%	2.3%
Maximum Intensity	8000 cd/m^2	10000 cd/m^2
Intensity @ 20 mA/cm^2	300 cd/m^2	460 cd/m^2

Wu, W.-C.; Yeh, H.-C.; Chan, L.-H.; Chen, C.-T.*Adv. Mater.* **2002**, *14*, 1072.
Yeh, H.-C.; Yeh, S.-J.; Chen, C.-T. *Chem. Commun.* **2003**, 2632.

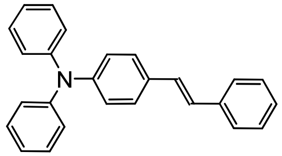
Structural Hindrance Prevents Fluorophores from Close Contact (via π-π Interaction) in the Solid State

A molecular design strategy in preventing fluorophores from emission quenching in the solid state

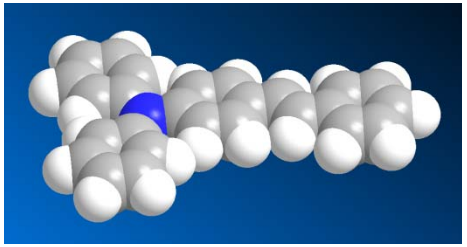




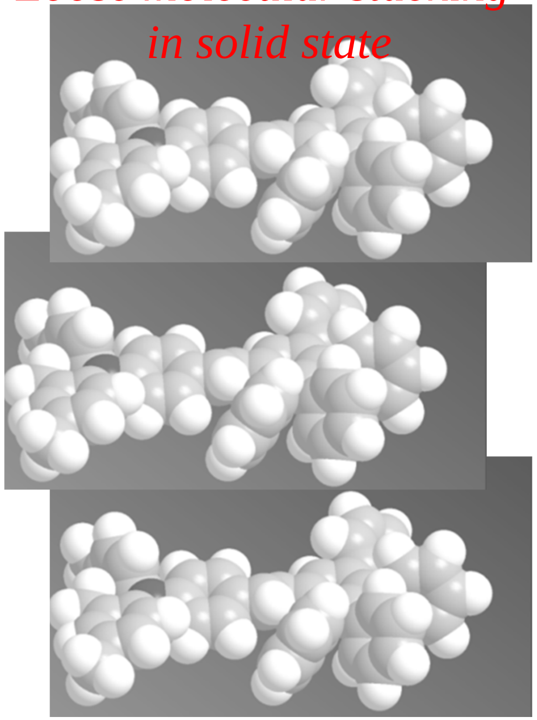
XTPS



Ph_2N-Stilbene

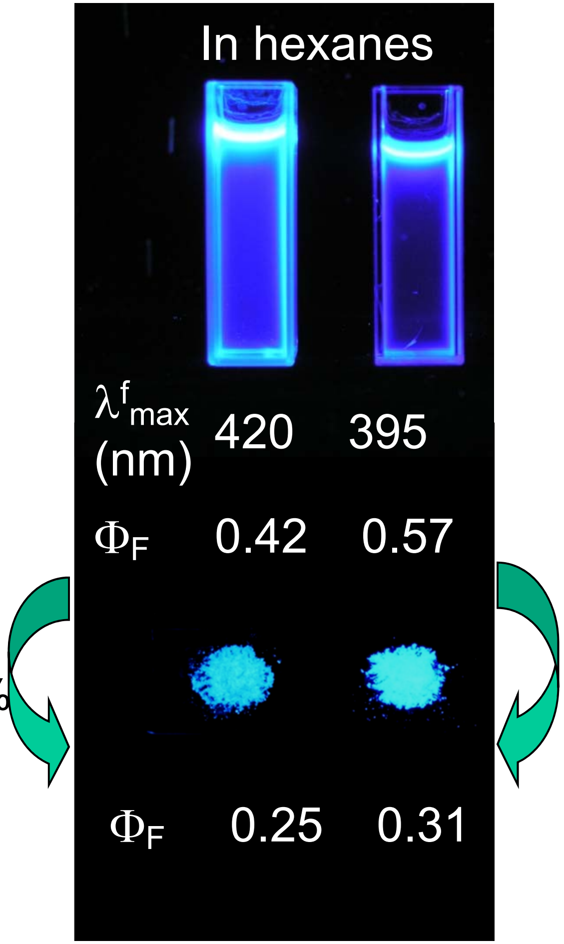


Loose molecular stacking in solid state



寬鬆堆疊

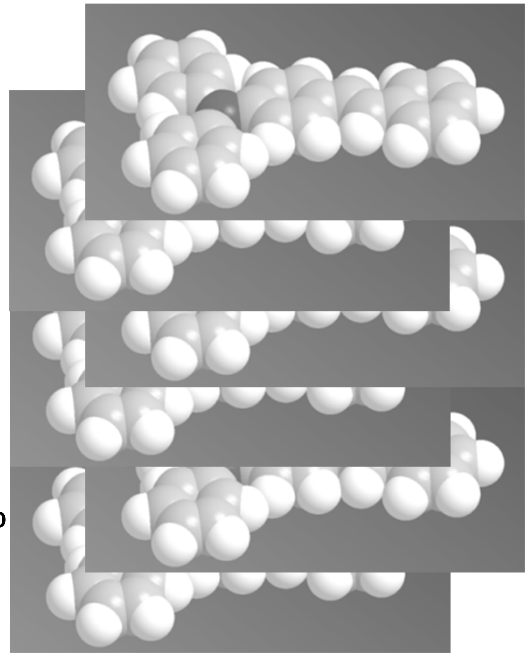
-40%



Tight molecular stacking in solid state

緊密堆疊

-46%

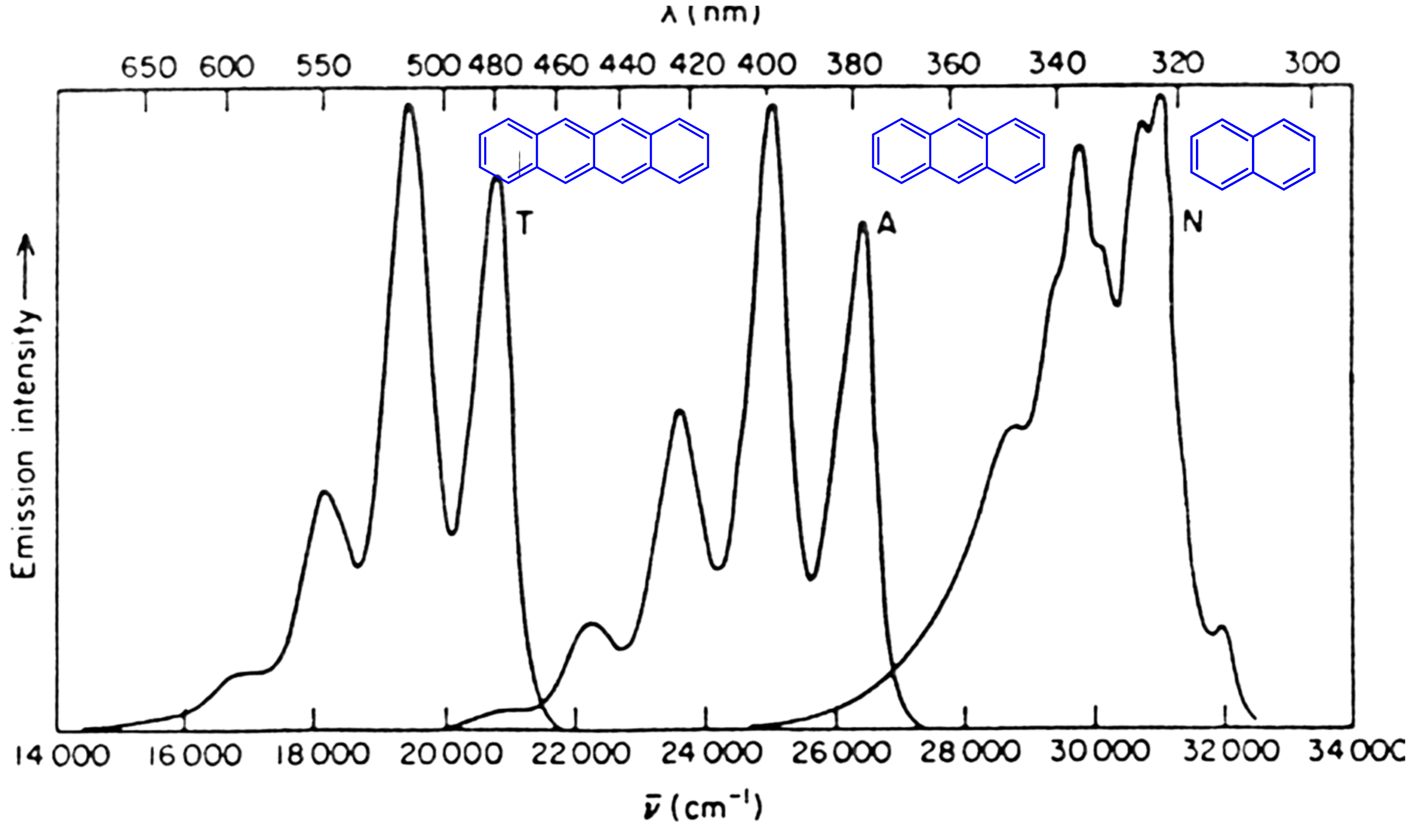


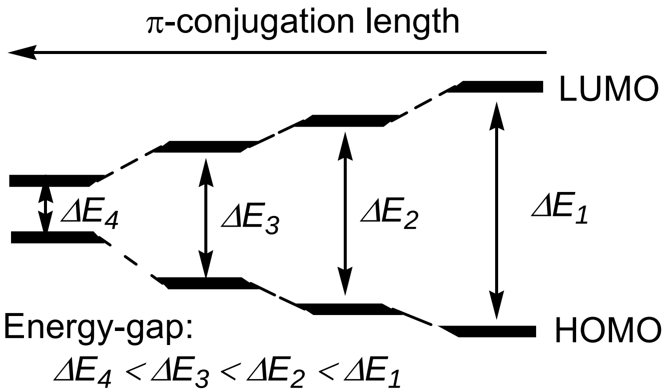
Chen, C.-T.; Chiang, C.-L.; Lin, Y.-C.; Chan, L.-H.; Huang, C.-H.; Tsai, Z.-W.; Chen, C.-T. *Org. Lett.* **2003**, *5*, 1261.

Yang, J.-S.; Chiou, S.-Y.; Liau, K.-L. *J. Am. Chem. Soc.* **2002**, *124*, 2518.

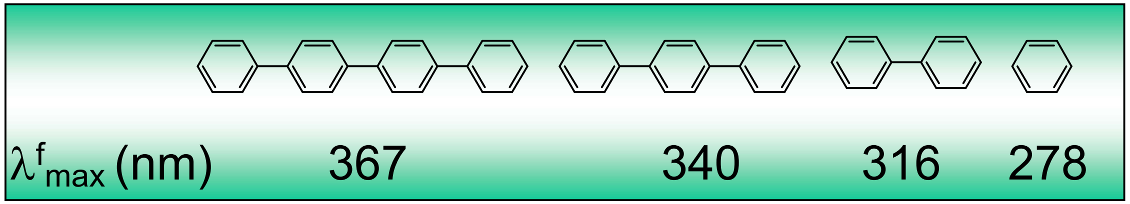
Color Tuning of Fluorescence

π-Conjugation length approach



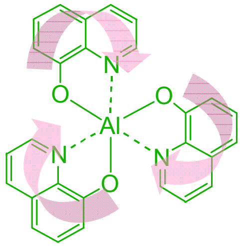


Guilbault, G. G., *Practical Fluorescence* 2nd ed., 1990.

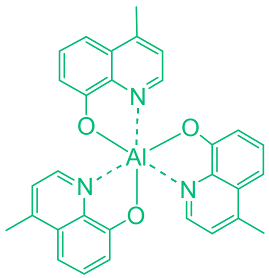


Fine Tuning Color of Alq_3

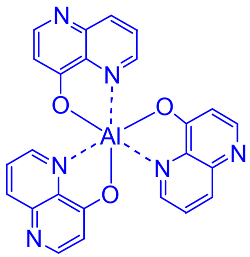
Electron donor-acceptor approach



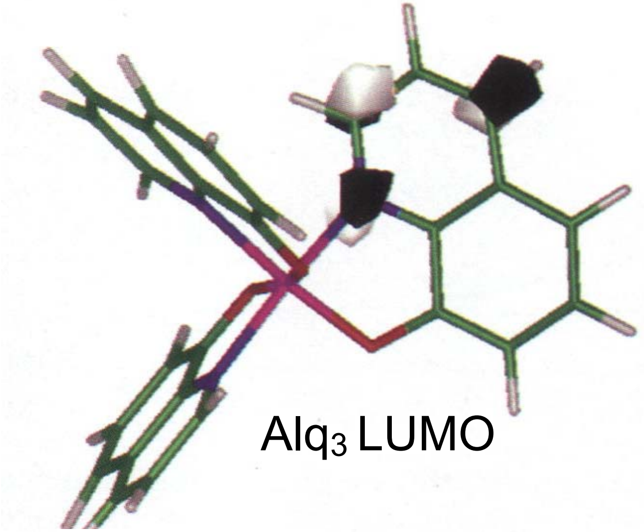
532 nm

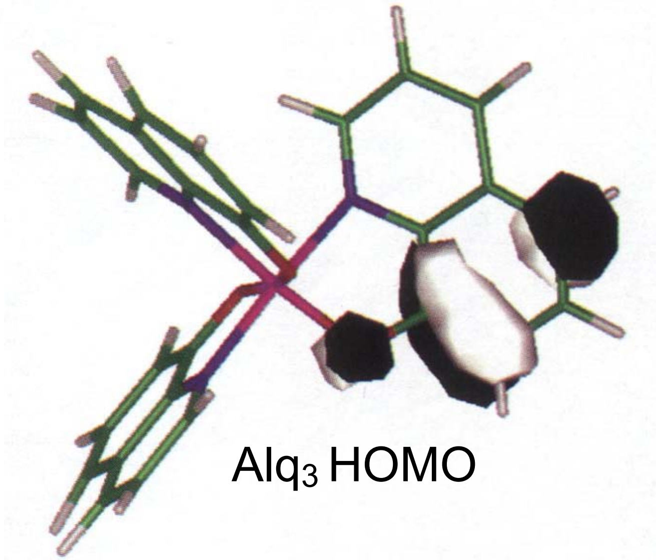


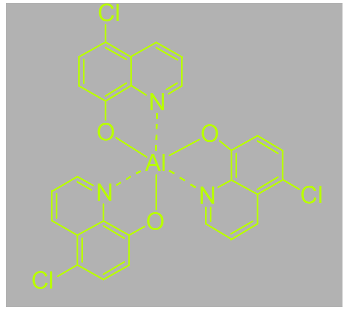
522 nm



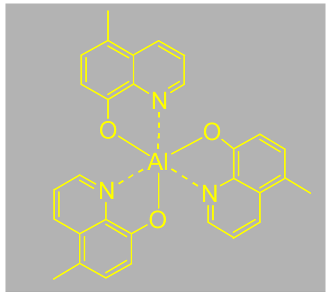
440 nm



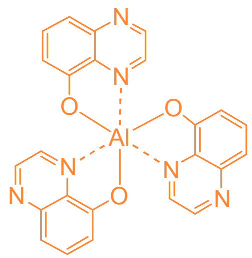




542 nm



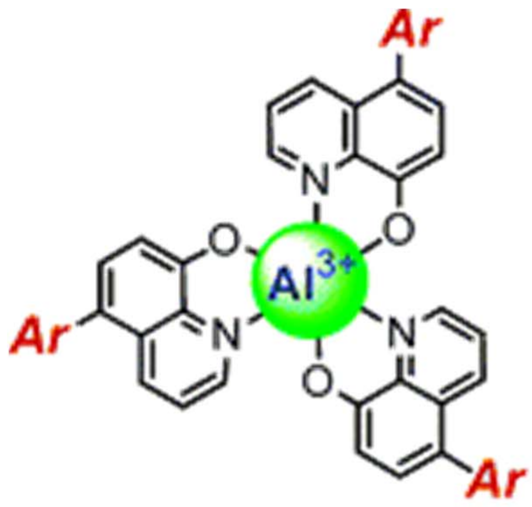
563 nm

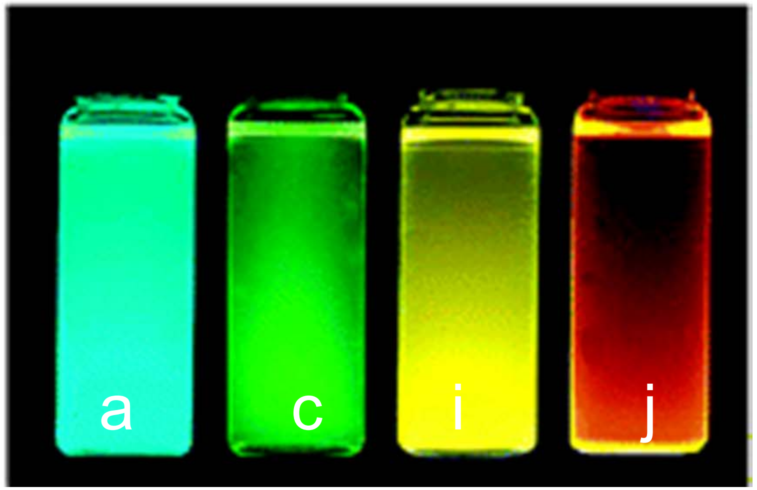


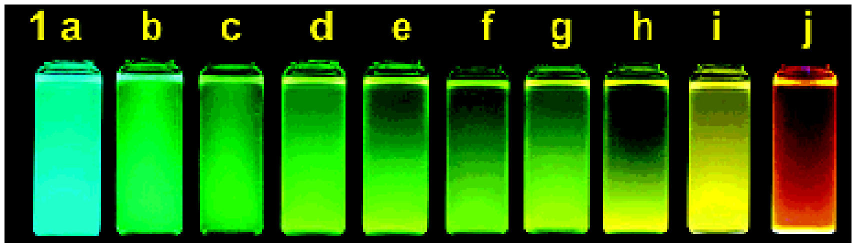
580 nm

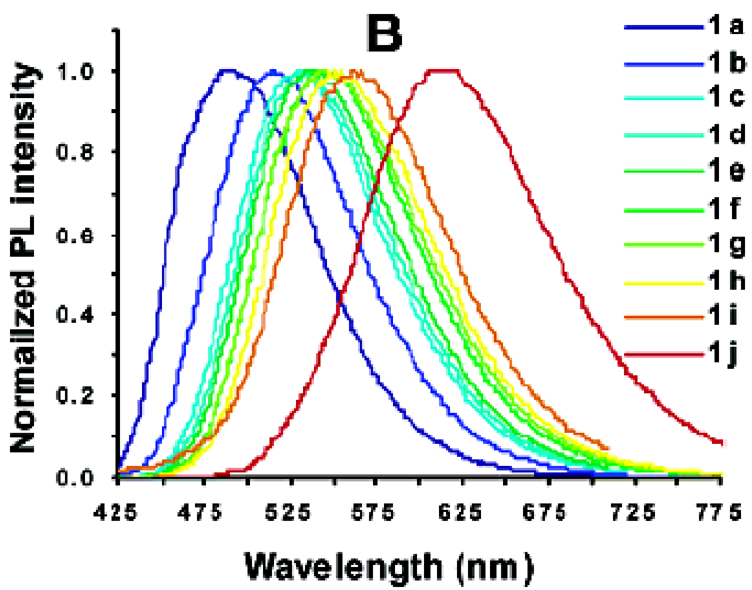
Burrows, P. E.; Shen, Z.; Bulovic, V.; McCarty, D. M.; Forrest, S. R.; Thompson, M. E. *J. Appl. Phys.* **1996**, *79*, 7991

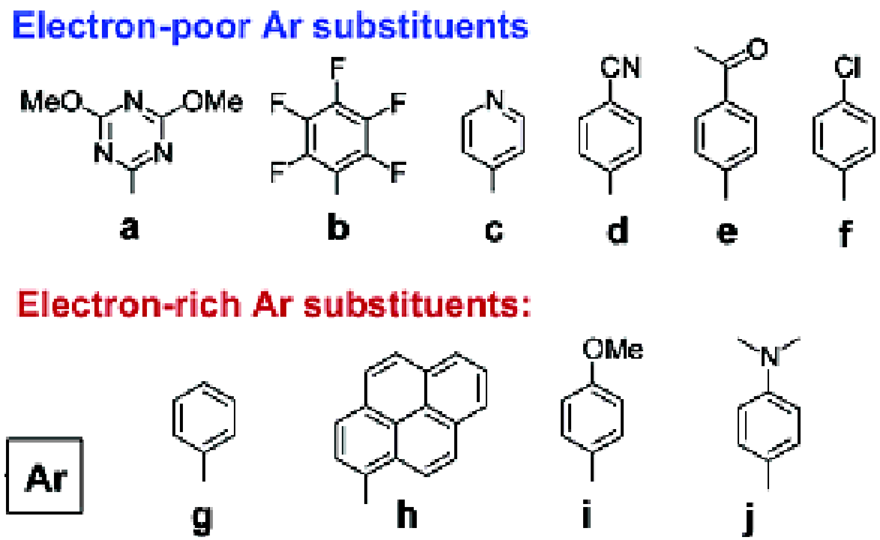
Chen, C. H.; Shi, J. *Coord. Chem. Rev.* **1998**, *171*, 161.





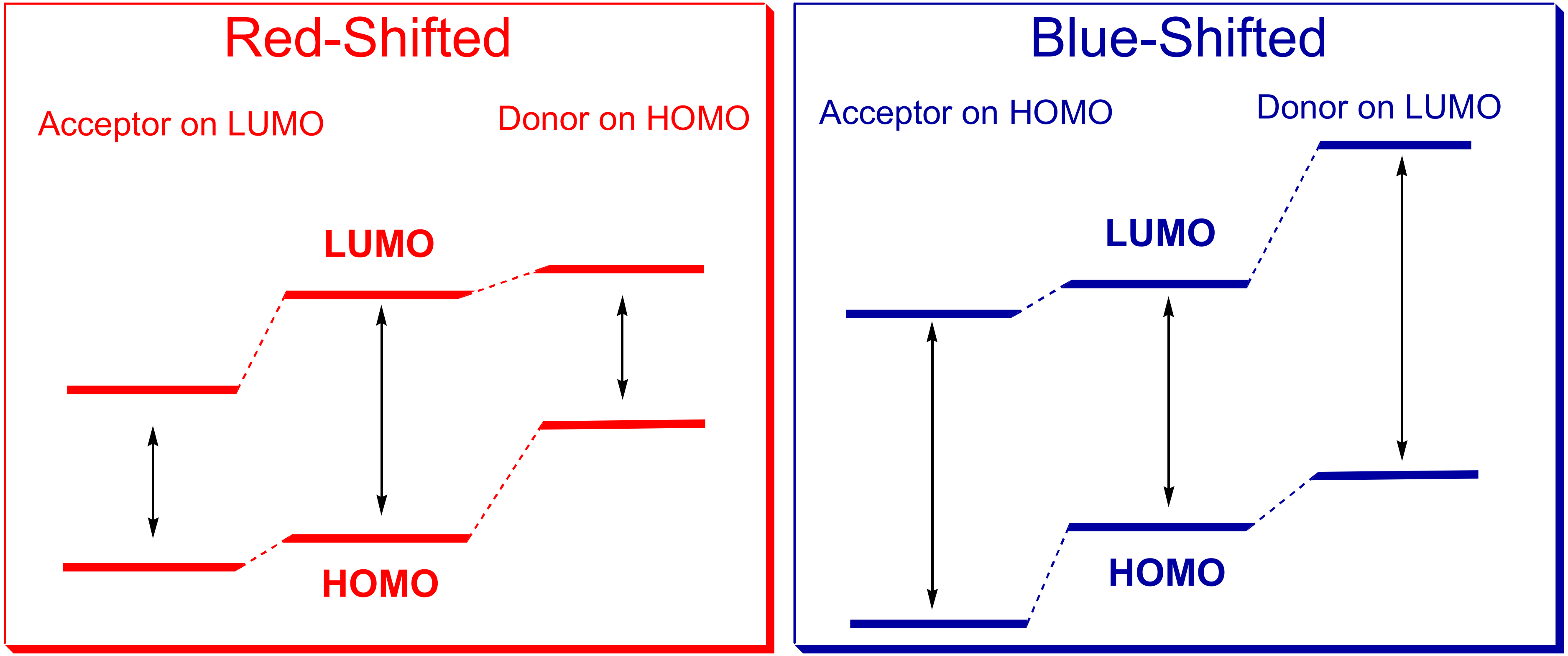






R. Pohl, V.A. Montes,† J. Shinar, P. Anzenbacher Jr.
J. Org. Chem. **2004**, *69*, 1723.

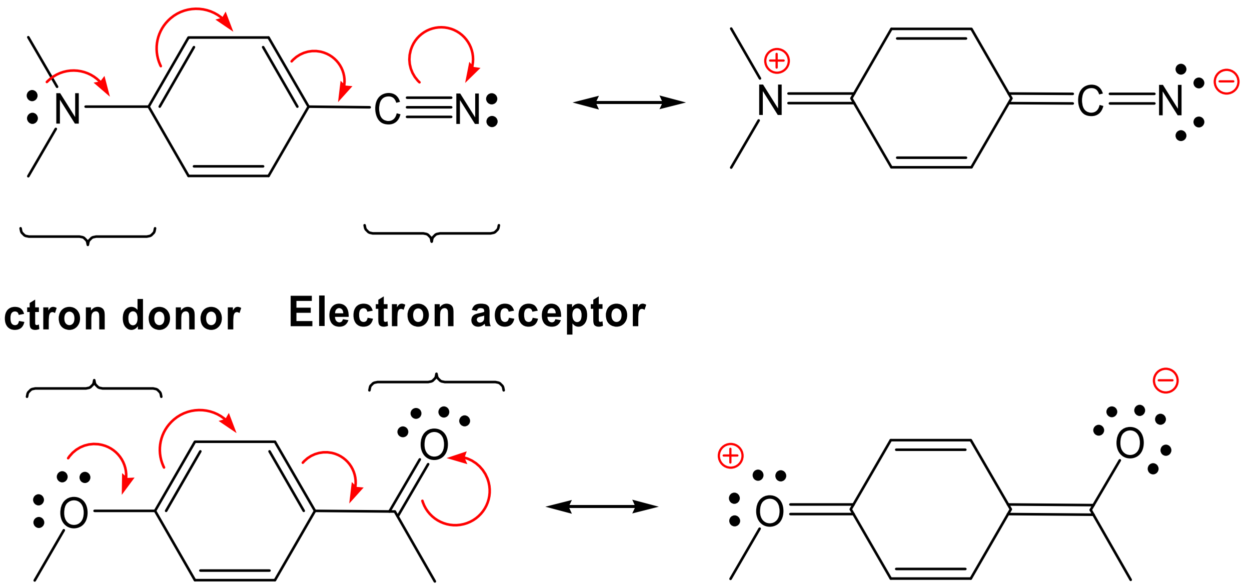
Tuning of Energy Gap by Donor and Acceptor



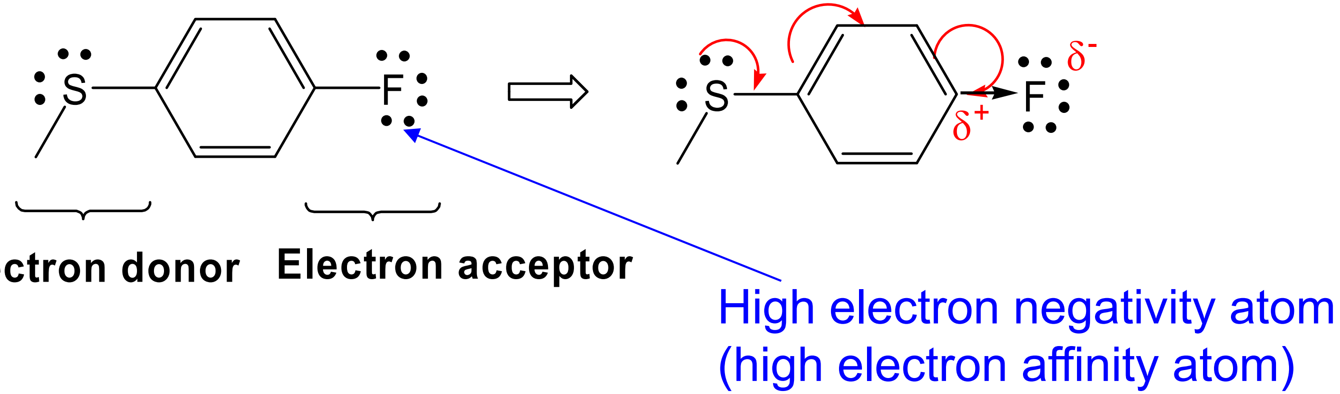
★ *Electronic donor always raises the energy level*

★ *Electronic acceptor always lowers the energy level*

Resonance Effect



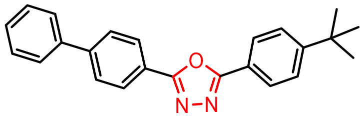
Inductive Effect



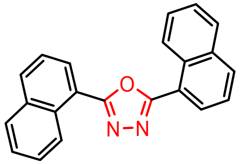
Heterocyclic Compounds as Electron-Transporting Materials for OLED

Electron-deficient structures can be as electron acceptors

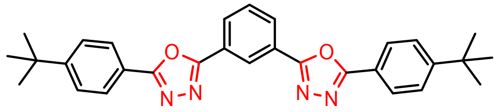
Oxadiazole



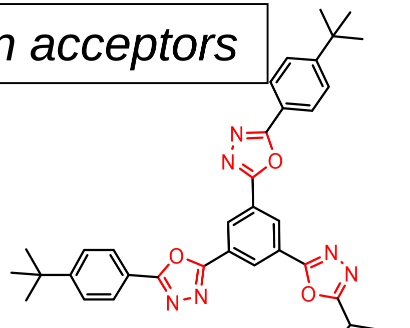
PBD



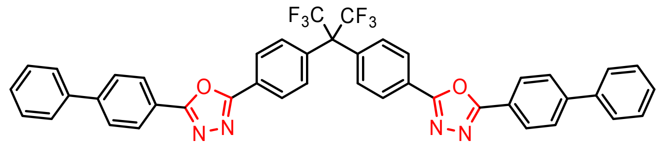
BND

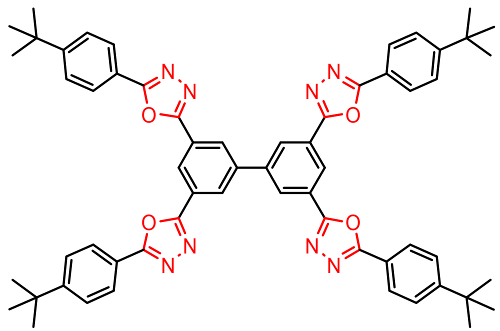


OXD-7

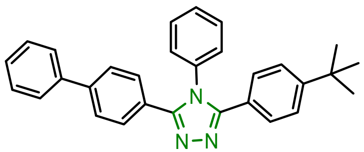


OXD-Star

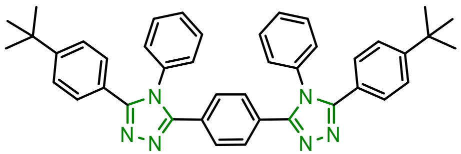




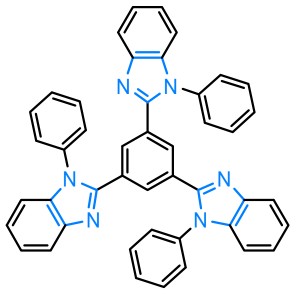
Triazole



TAZ

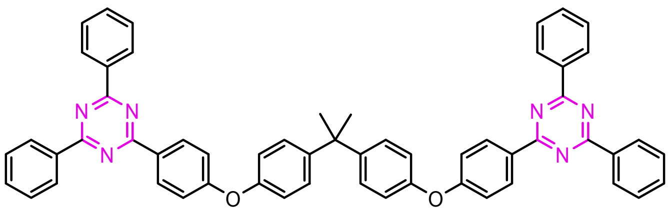


Phenylbenzimidazole

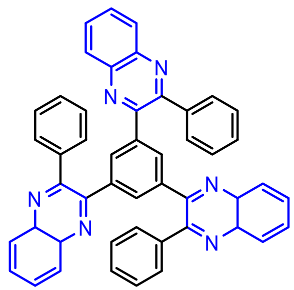


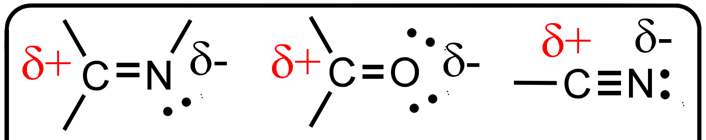
TPBI

Triazine



Phenylquinoxaline





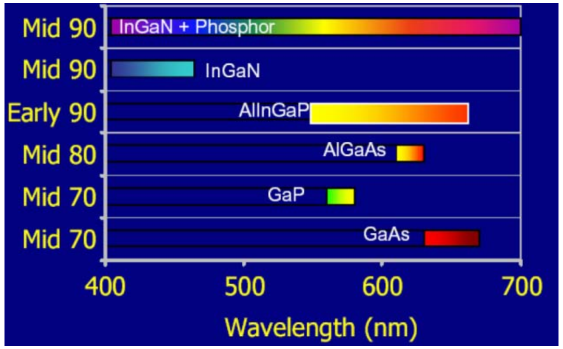
Electron deficient center (δ+)
facilitating electron transport

White Light Illuminating and Energy 白光照明與能源

Lighting accounts for approximately 22% of the electricity consumed in buildings in the US, with 40% of that amount consumed by inefficient (~15 lm/W) incandescent lamps.

Nature, 2006, 440, 908.

The latest entrant to the lighting market is the pea-size light-emitting diode (LED). LEDs can last as long as ten years, but use less than 25% electric power of tungsten (incandescent) light bulbs. However, LED lighting is much more costly than the traditional lightings.



White LEDs (for solid state lighting) are available only recently (since mid 90's) because of the lack of short wavelength (blue) InGaN LED

Isamu Akasaki, Hiroshi Amano, Shuji Nakamura

"For the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources" The Nobel Prize in Physics 2014

THE END OF THE LIGHT BULB

Global warming, ever-expanding energy demand pave way for NEW LIGHTING TECHNOLOGIES

JEFF JOHNSON, C&EN WASHINGTON

THERE'S A REVOLUTION going on in lighting. And some say it's about time.

Two hundred years ago, British scientists forced electrons through a strip of platinum and laid the groundwork for what would become the first incandescent light. In 1870s and '80s, Thomas Edison and several competitors put the bulb on a path to commercialization and changed the world.

Today, for most people who have electric lights in their homes, illumination still comes from electricity run through a wire filament, enclosed and protected in a glass bulb.

Cheap, simple, easy to install, and manufactured by the billions, the incandescent light bulb is a staple of modern life. Unfortunately, 90 to 95% of the energy it consumes goes to heat, not light. Billions of bulbs wasting trillions of watt-hours of electricity is always bad, but particularly so in a time of increasing concern over climate change—when electrical power generation contributes more than one-third of the greenhouse gases that are changing Earth's environment.

Lighting is a big player in the global-warming game. Illumination eats up about 19% of global power, and energy consumption for lighting is projected to grow by 60% over the next 25 years, according to the International Energy Agency (IEA).

In the U.S., about 22% of the total electricity demand is used for lighting. Of this 22%, half is used in lighting commercial businesses, 27% is for homes, 14% for industry, and 8% for outdoor applications, according to the Department of Energy. About $58 billion a year is spent on lighting.

Since homes remain highly dependent on inefficient incandescent lighting, residences are responsible for the greatest amount of wasted energy. They also have the biggest potential for savings, however, thanks to alternatives to traditional bulbs, which are growing in availability and impact. These bulbs could disrupt the definition of lighting.

Compact fluorescent lights (CFLs) draw only about 20 to 25% of the energy of incandescent bulbs for a comparable amount of light generated. Although they cost about four times more, CFLs last 10 times longer than incandescent bulbs and make back their price severalfold in energy savings and extended life.

Solid-state technologies are coming on too, with light-emitting diodes (LEDs) finding growing general lighting applications. LEDs are as efficient as CFLs and last for decades but are now too expensive to compete on all fronts with a light bulb. Organic light-emitting diodes (OLEDs) are waiting in the wings, providing a thin sheet of pure white light.

AT THEIR CORE, CFLs and LEDs are completely different technologies from that of incandescent bulbs. They do not rely on incandescence or intense heat to produce visible light. Instead, they produce visible light waves by using energy given off from the transition of electrons from one energy level to another.

Residential lighting consumes about 16% of electricity used in U.S. homes, says John Cymbalsky, operations research analyst with DOE Energy Information Administration. This works out to 6% of all U.S. electricity. Using CFLs or solid-state lighting would save about 4% of this total electricity, savings which would avoid building the equivalent of roughly 20 new 1,000-MW nuclear power plants.

But getting people to shift from the common light bulb is tough. It is hard to beat an incandescent light for low cost and ease in replacement—buy it for a half-a-buck, screw it in, flip the switch, and forget about it. Even so, Wal-Mart, Home Depot, and other big-box retailers; several utilities; and DOE have all embarked on programs to kill off the incandescent light.

Last year, Wal-Mart announced its intention to sell 100 million CFLs by the end of 2007. In October, it crowed that it had already met its goal.

Wal-Mart just didn't stick the lights on a shelf and hope, explains company spokeswoman Tara Raddohl. It marketed the CFLs under its own brand Great Value, sold them below competitors' prices, prominently displayed the new stock, set up interactive demonstrations to explain the lights' attributes, and promoted CFL sales as part of the company's new sustainable products program.

Wal-Mart even underscored its sales and sustainability programs by announcing its intention to pressure its manufacturer to reduce the small amount of mercury in CFLs. Mercury vapors in fluorescent lighting emit ultraviolet light when hit with a beam of electrons. The UV energy excites a phosphor on the inside surface of the glass

HEAT, NOT LIGHT Incandescent lights define household lighting. Dependable, familiar, and based on a 100-year-old technology, incandescents last for up to 1,000 hours, cost 50 cents, and waste 95% of their output energy as heat, not illumination.

ROBERT SPRIGGS/SHUTTERSTOCK

COMPACT FLOURESCENT LIGHTS CFLs last for 10,000-plus hours, use 20 to 25% of the energy of an incandescent light and usually cost $2.00 to $3.00. Despite their price, manufacturers claim a lifetime saving of at least $50 due to reduced energy use and extended life as compared with incandescent lights.

BILL FEHR/SHUTTERSTOCK

PEA-SIZED Light-emitting diodes are new to general lighting. Used mostly for traffic lights, brake lights, flashlights, and exit signs, they are making inroads into commercial and residential lighting. LEDs last decades and use less than 25% of the energy needed for incandescent lights but remain too expensive to outcompete common light bulbs in many applications.

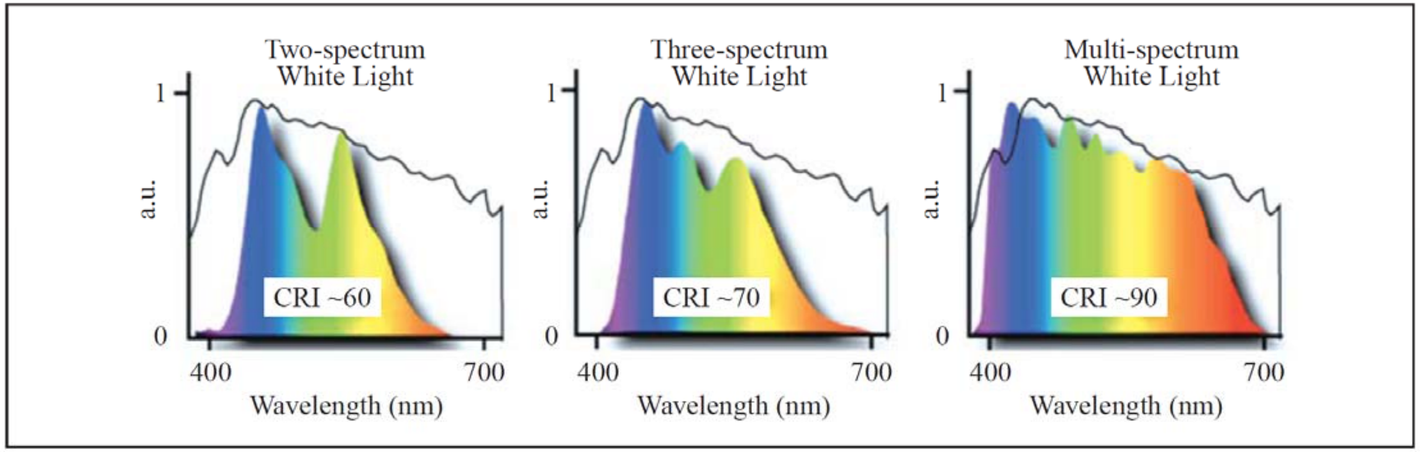
ZHOLUDOV SERHIJ/SHUTTERSTOCK

CEN-ONLINE.ORG 46 DECEMBER 3, 2007

C&EN CHEMICAL & ENGINEERING NEWS

*C & E News **2007**, December 3, p.46.*

Effect of Color Rendering Index (CRI) of Light Source



CRI of Different Light Sources

100-watt incandescent (Tungsten light bulb)	100
Metal halide lamp 5400k	93
Daylight fluorescent lamp	79
Cool white linear fluorescent tube	65
Warm white fluorescent tube	55
High pressure mercury	17-45
High pressure sodium lamp	25
Monochromic Sodium D-line	～0

以LED為光源的燈具照射下，物件色彩豔麗度不足
Poor color gamut

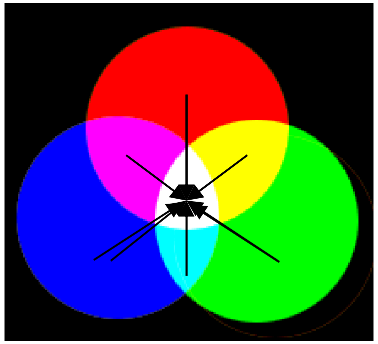
Natural daylight and any light source approximating a blackbody radiation are assigned a CRI of 100.

周卓煇 工業材料雜誌 ***2010****, 282, Jun, 167-173.*

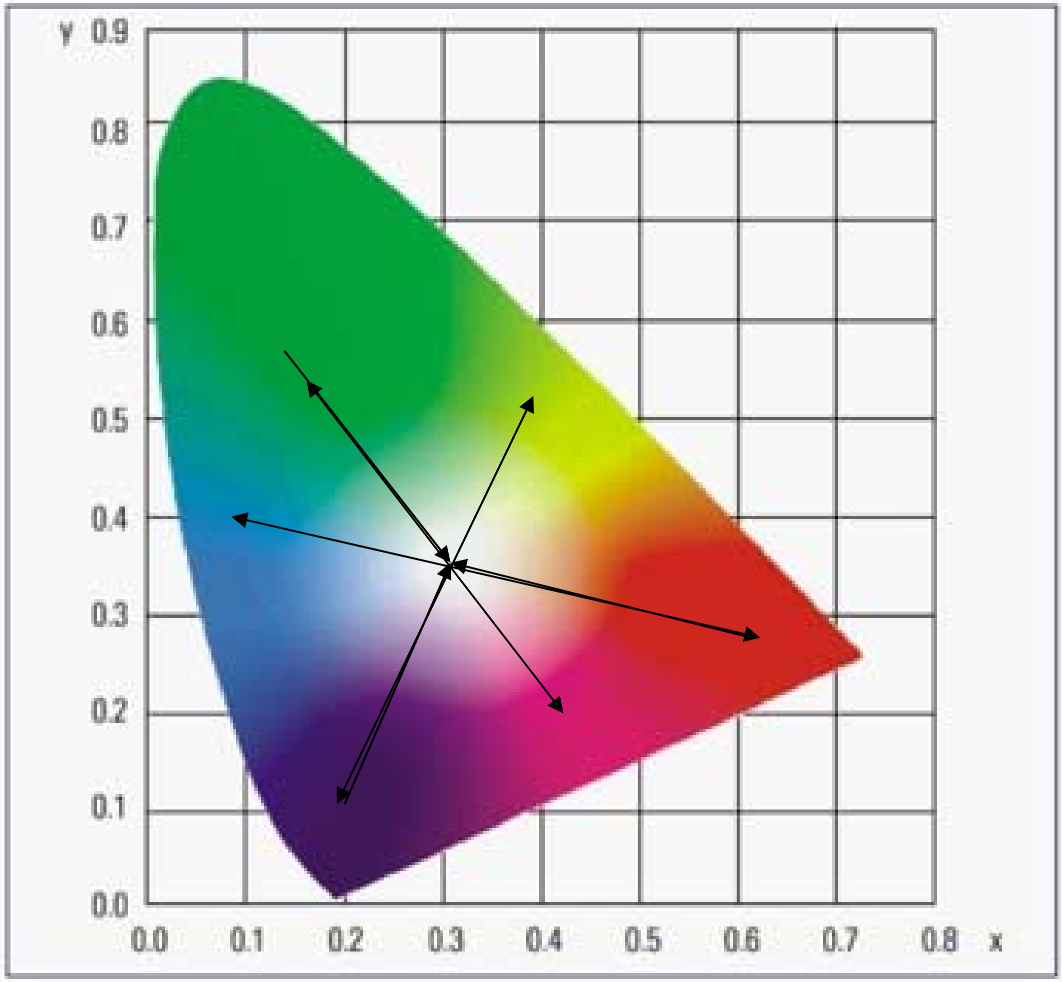
http://sclp.lightingresearch.org/technicalGuide/terminology/cri.asp?section=1.2.6

Colors, Including White (Colorless!)

Color lights combine by addition



1931 CIE Chromaticity Diagram



Three primary colors：

Red/Green/Blue

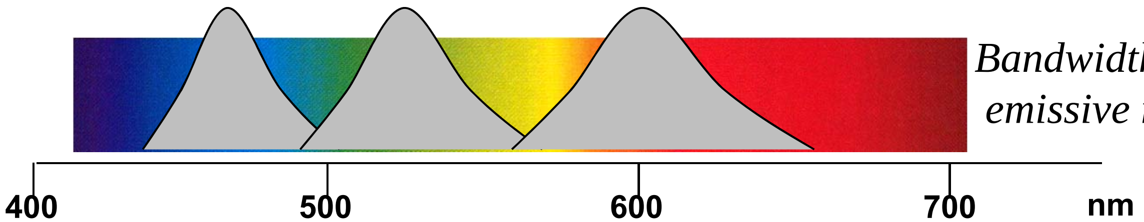
Addition of color:

R+G→Yellow

R+B→Magenta

G+B→Cyan

R+G+B→



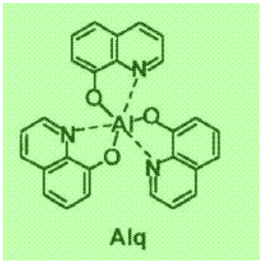
Bandwidth of any single color emissive material is < 100 nm

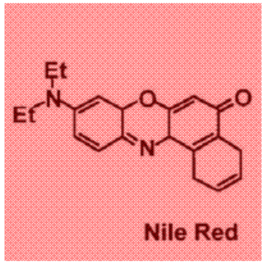
The First Demonstration of White OLEDs

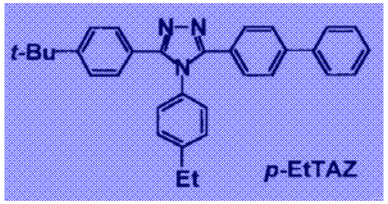
1332 **Multilayer White Light–Emitting Organic Electroluminescent Device** SCIENCE • VOL. 267 • 3 MARCH 1995

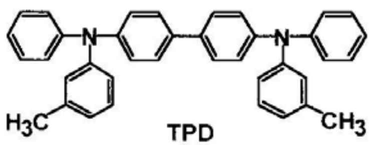
Junji Kido, Masato Kimura, Katsutoshi Nagai

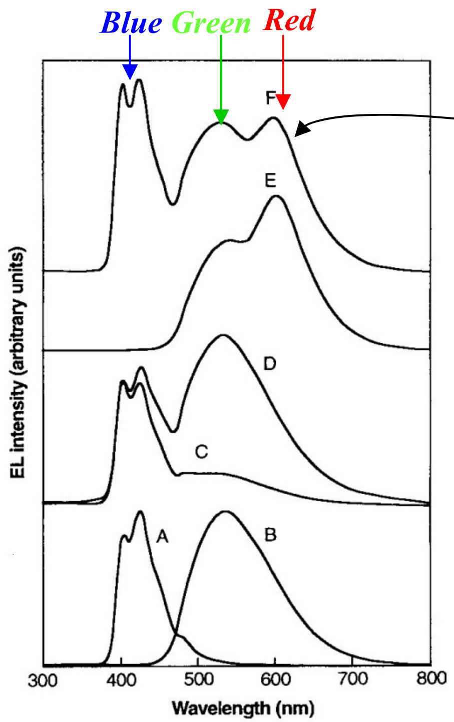
Department of Materials Science and Engineering, Yamagata University, Yonezawa, Yamagata 992, Japan.

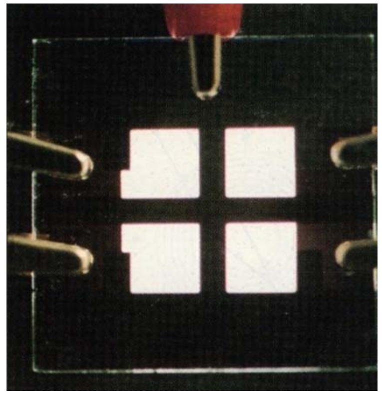


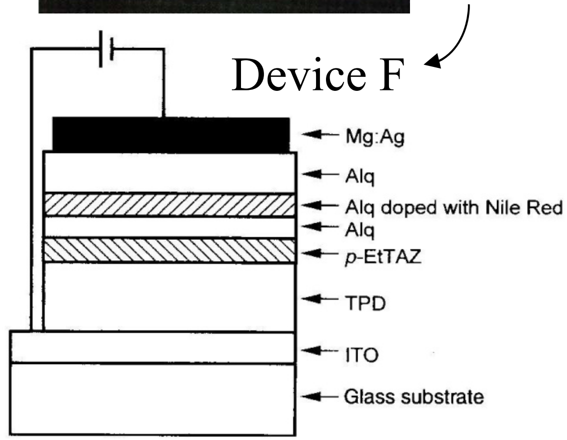












300 cd/m^2, 0.5 lm/W
@ 12 V and ~20 mA/cm^2

A : ITO/TPD(50 nm)/p-EtTAZ(50 nm)/Mg:Ag
B : ITO/TPD(50 nm)/Alq_3(50 nm)/Mg:Ag
C : ITO/TPD(40 nm)/p-EtTAZ (5 nm)/Alq_3(50 nm)/Mg:Ag
D : ITO/TPD(40 nm)/p-EtTAZ (3 nm)/Alq_3 (50 nm)/Mg:Ag
E : ITO/TPD(40 nm)/Alq_3(5 nm)/Alq_3:Nile Red (1%, 5 nm)/Alq_3(40 nm)/Mg:Ag
F : ITO/TPD(40 nm)/p-EtTAZ(3 nm)/Alq_3(5 nm)/Alq_3:Nile Red (1%, 5 nm)/Alq_3 (40 nm)/Mg:Ag

Three-color-composed white

1 host containing 1 dopant

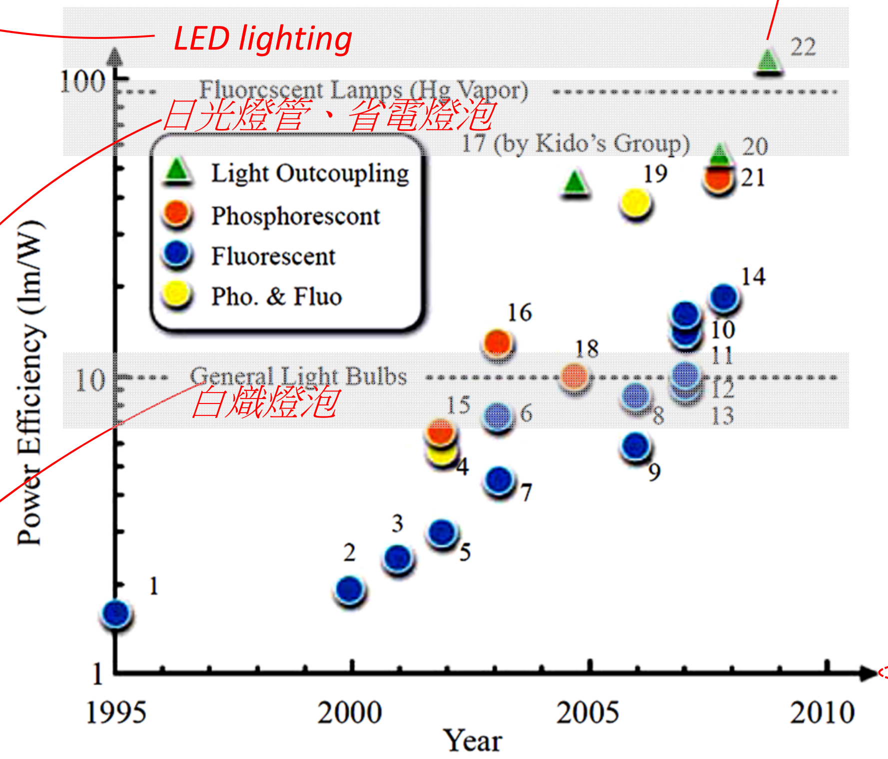
Advantage and Disadvantage of White OLEDs Lighting Application

High efficiency but poor heat dissipation (due to the small crystal size) reducing its performance to less than half

---- it is relatively expensive (epitaxial crystal growth process)

☆ Phosphorescence materials are necessary for the outperformance of WOLED in terms of efficiency

---- Light output enhanced WOLED is also needed



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3. Y. T. Tao, et al. Applied Physics Letters 79, 25 (2001)
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11. J. H. Jou. et al. Org. Electronics 8, 735 (2007)
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17. R. F. Service in Science 310, 1762 (2005)
18. S. Tokito, et al. Current Applied Physics 5, 331 (2005)
19. S. R. Forrest, et al. Nature 440, 13 (2006)
20. S. R. Forrest, et al. Nature Photonics 2, 483 (2008)
21. J. Kido, et al. Adv. Mater. 20, 4189-4194 (2008)
22. Sebastian Reineke, et al. Nature 459, 14 (2009)

Toxic content of mercury, the heavy metals in fluorescence powder, and fragile

Low efficiency, high heat, fragile, short lifetime, but very cheap

Jwo-Huei Jou (周卓煇) *Industrial Materials (工業雜誌)* **2010**, *282 (June),* 167-173.

Adv. Mater. 2008, 20, 4189–4194

Highly Efficient Organic Blue-and White-Light-Emitting Devices Having a Carrier- and Exciton-Confining Structure for Reduced Efficiency Roll-Off**

ADVANCED MATERIALS

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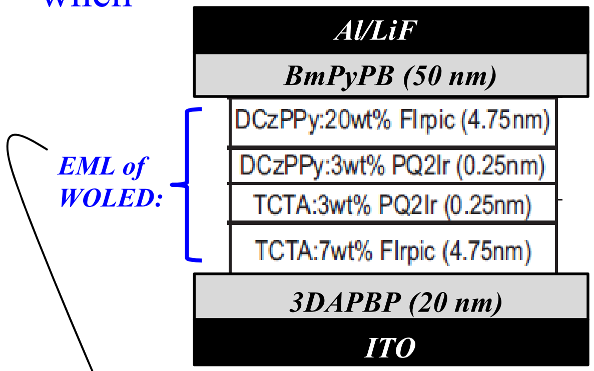
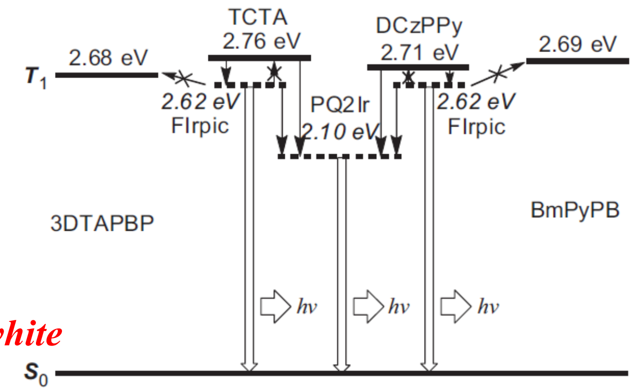
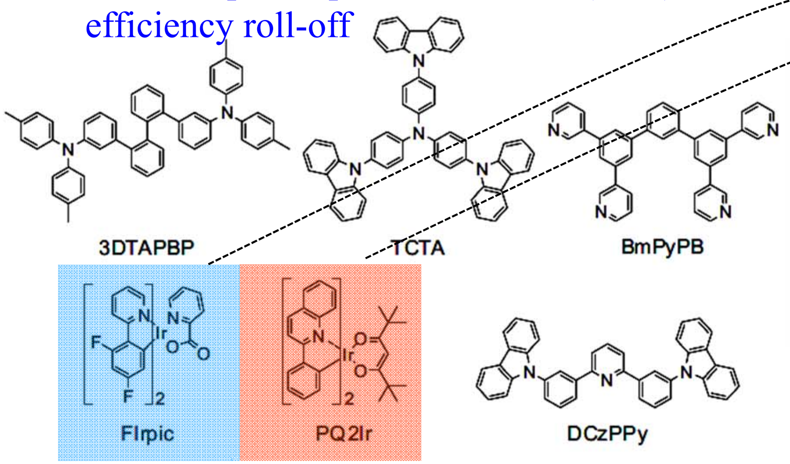
The improved efficiency and reduced efficiency roll-off at high luminances should arise from the precise confinement of FIrpic triplet excitons within the emissive layers. Generally, triplet excitons have long diffusion lengths. Good confinement of triplet excitons within the emissive layers can be achieved when all corresponding materials, i.e., the host materials and the adjacent HTM and ETM, have higher triplet energy levels than that of the triplet emitter.

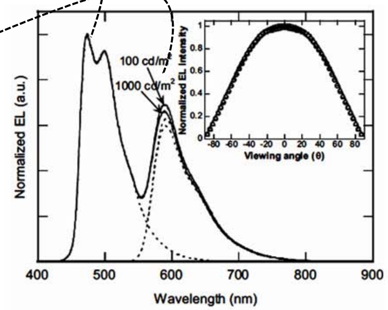


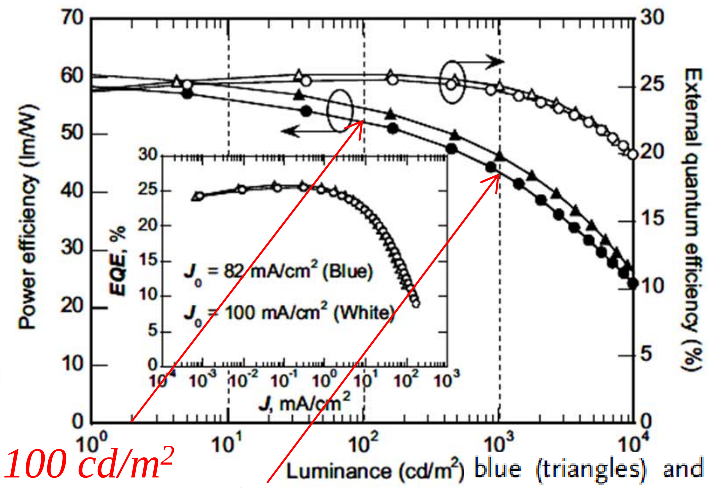


➡ Spread out phosphorescence emitters (in multiple layers) reduce triplet-triplet annihilation (TTA) and alleviate efficiency roll-off

CRI~68
Two-color-composed white







blue (triangles) and white (circles) OLEDs

53 lm/W @ 100 cd/m²
44 lm/W @ 1000 cd/m²

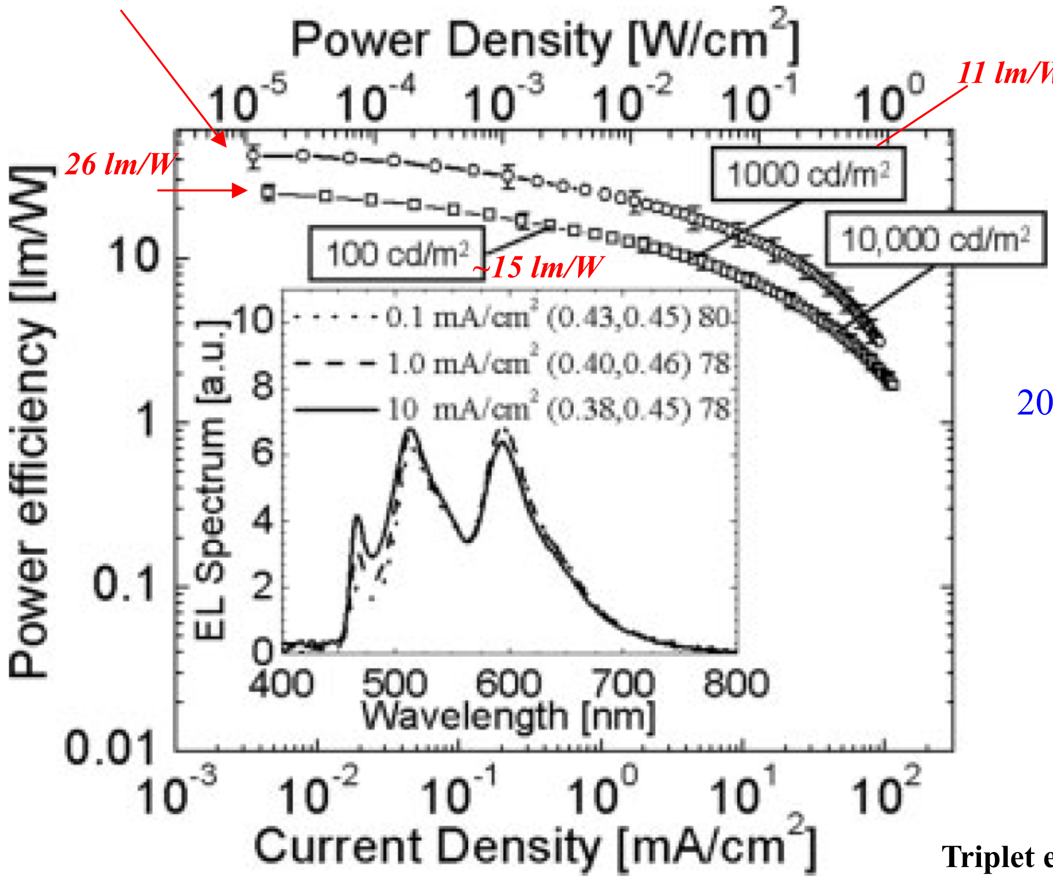
High Efficiency All Phosphorescence WOLEDs

42 lm/W (with lamp lighting fixture)

26 lm/W

11 lm/W

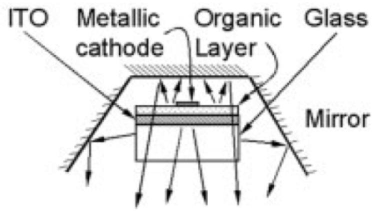
~15 lm/W



Quite signifant efficiency roll-off

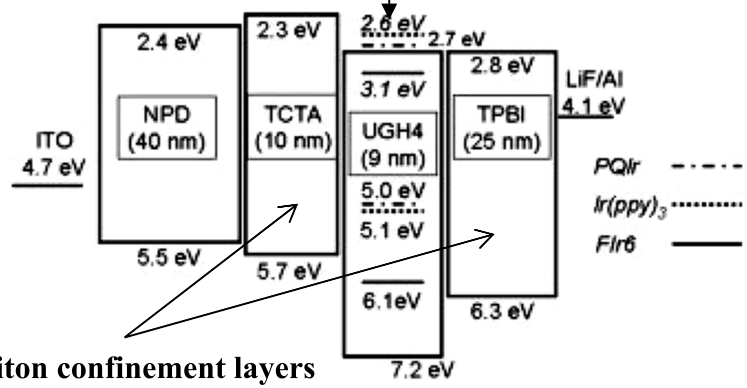
➡ *At lighting condition (>1000 cd/m²), without lamp lighting fixture, power efficiency (11 lm/W) is insufficient for practical usage*

Lamp lighting fixture

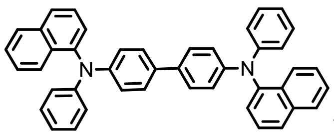


20 wt% FIr6; 0.5 wt% Ir(ppy)$_3$; 2 wt% PQIr in UGH4

Triple doped phosphorescent emission layer

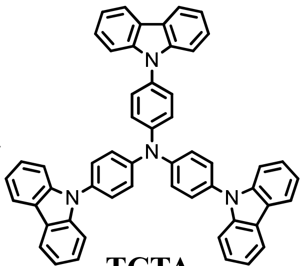


Triplet exciton confinement layers



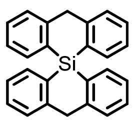
NPB

Hole transport



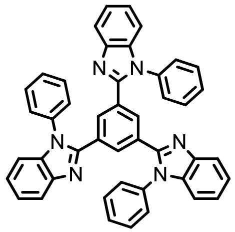
TCTA

High triplet state hole transport



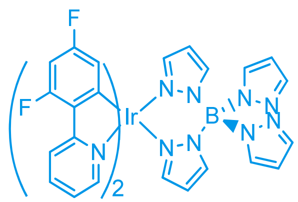
UGH4

Phosphorescence dopant host

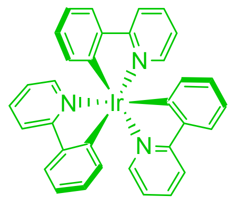


TPBI

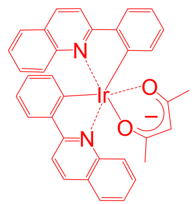
Electron transport



FIr6



Ir(ppy)$_3$



PQIr

Forrest, S. R. et al *Adv. Mater.* **2004**, *16*, 624.

nature Vol 459|14 May 2009| 234

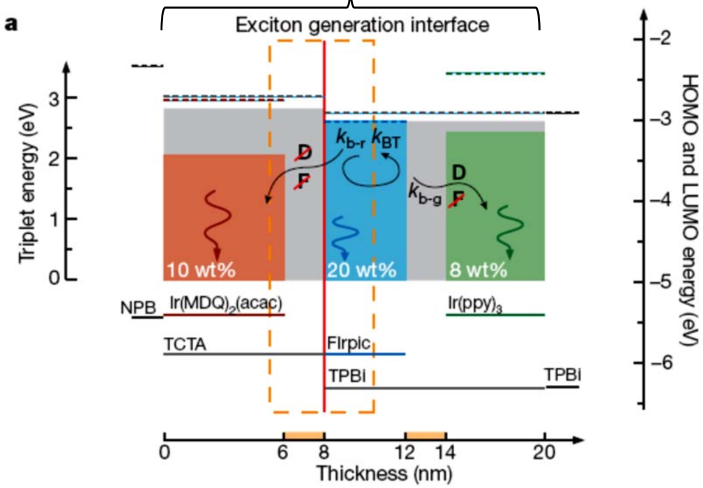
White organic light-emitting diodes with fluorescent tube efficiency

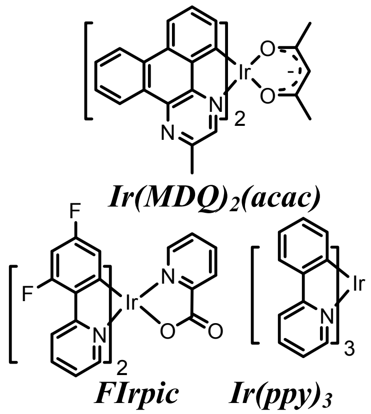
60~70 lm/W

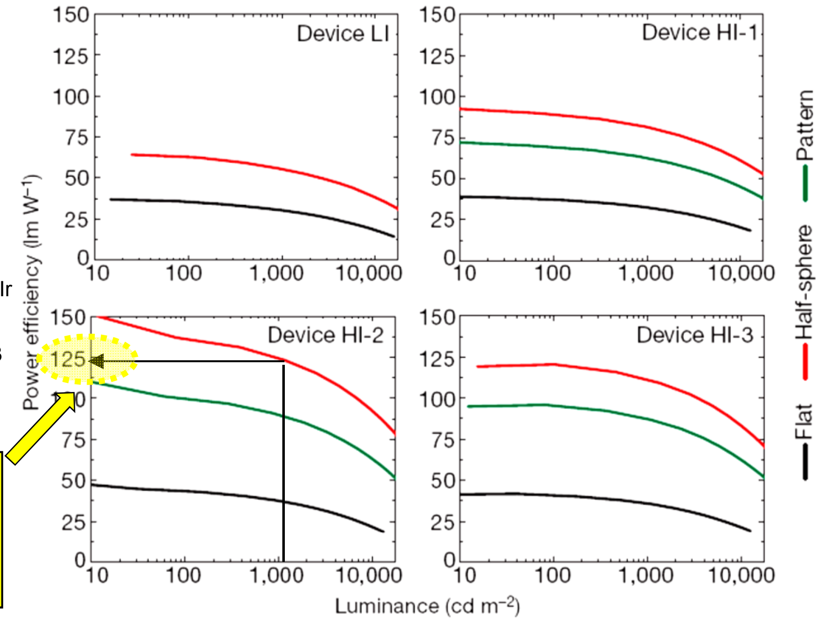
[1]Institut für Angewandte Photophysik, George-Bähr-Strasse 1, D-01062 Dresden, Germany.

Sebastian Reineke[1], Frank Lindner[1], Gregor Schwartz[1], Nico Seidler[1], Karsten Walzer[1], Björn Lüssem[1] & Karl Leo[1]

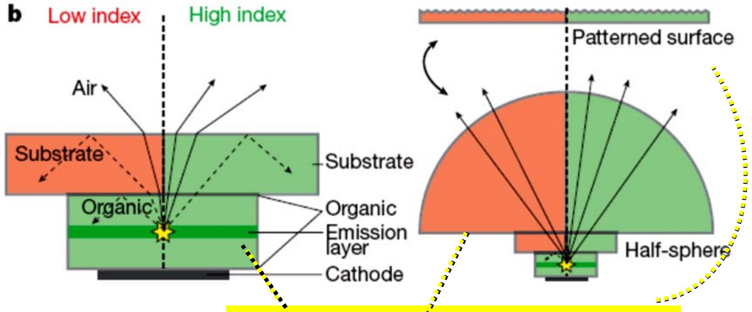
ITO/MeO-TPD:NDP-2 (60 nm, 4%)/NPB (10 nm)/emission layer/TPBi(10 nm)/Bphen: Cs/Ag (100 nm)





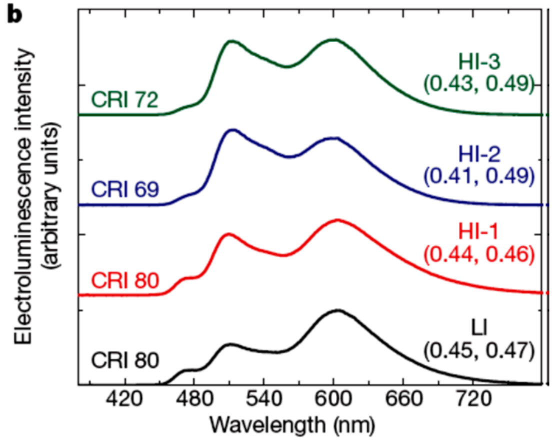


124 lm/W @1000 cd/m^2 (η_{EXT} 46%)

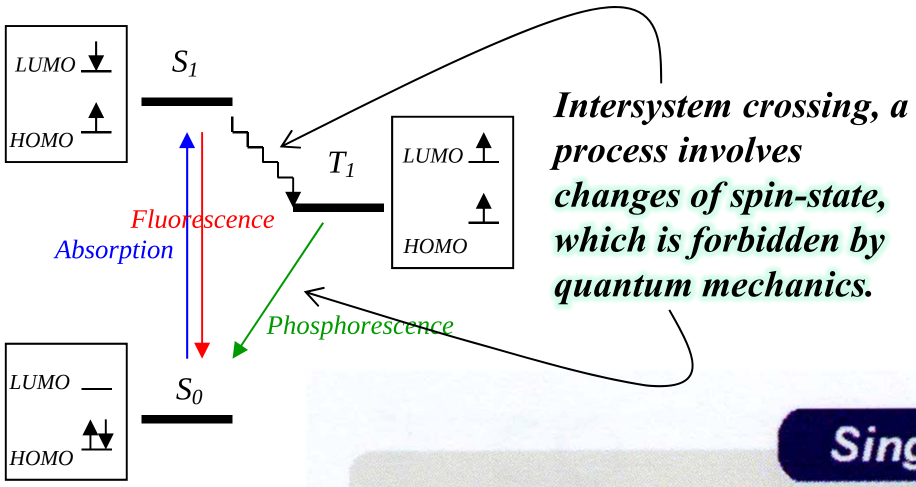


Flat, Half-sphere, Pattern

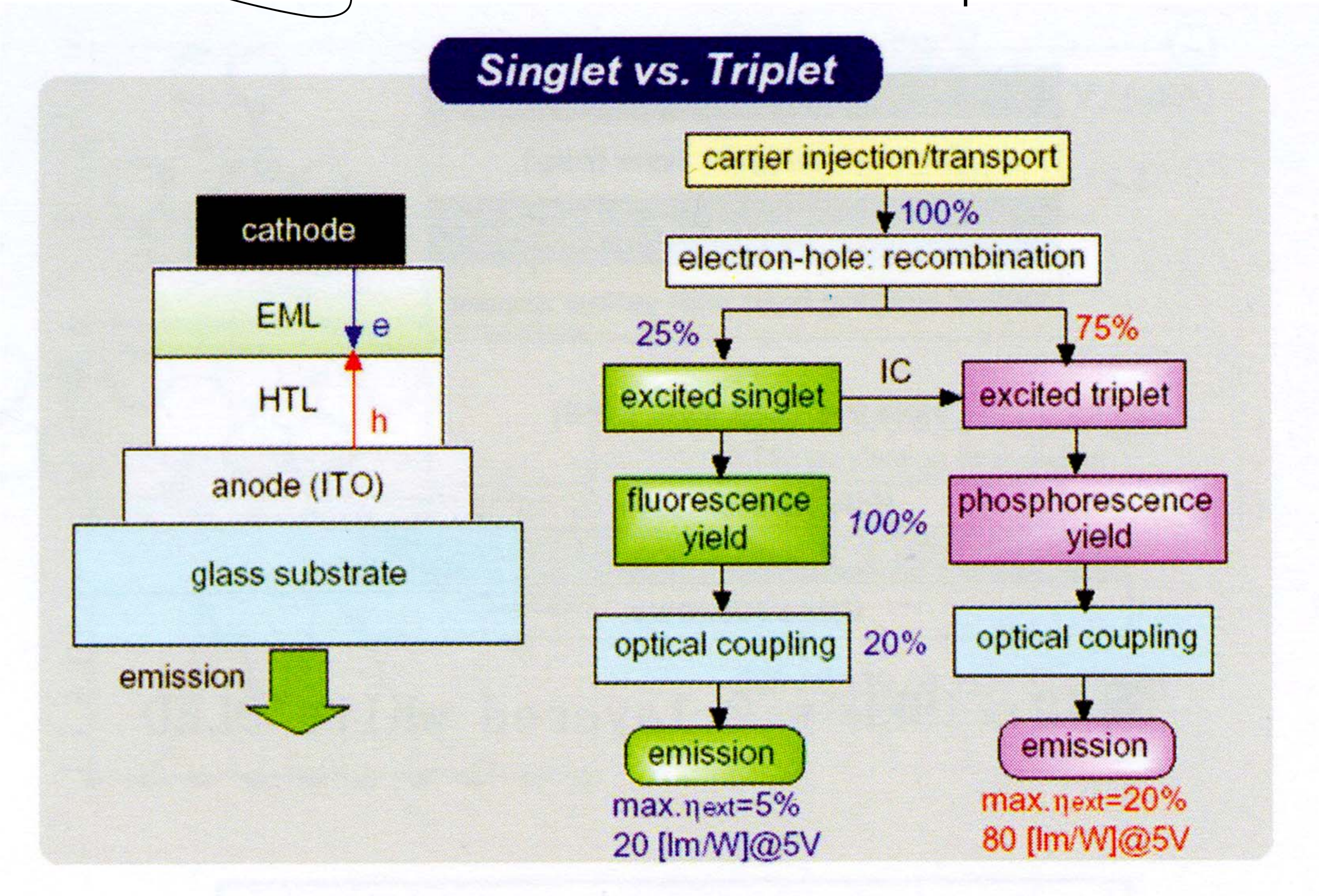
Optical methods for light out-coupling enhancement



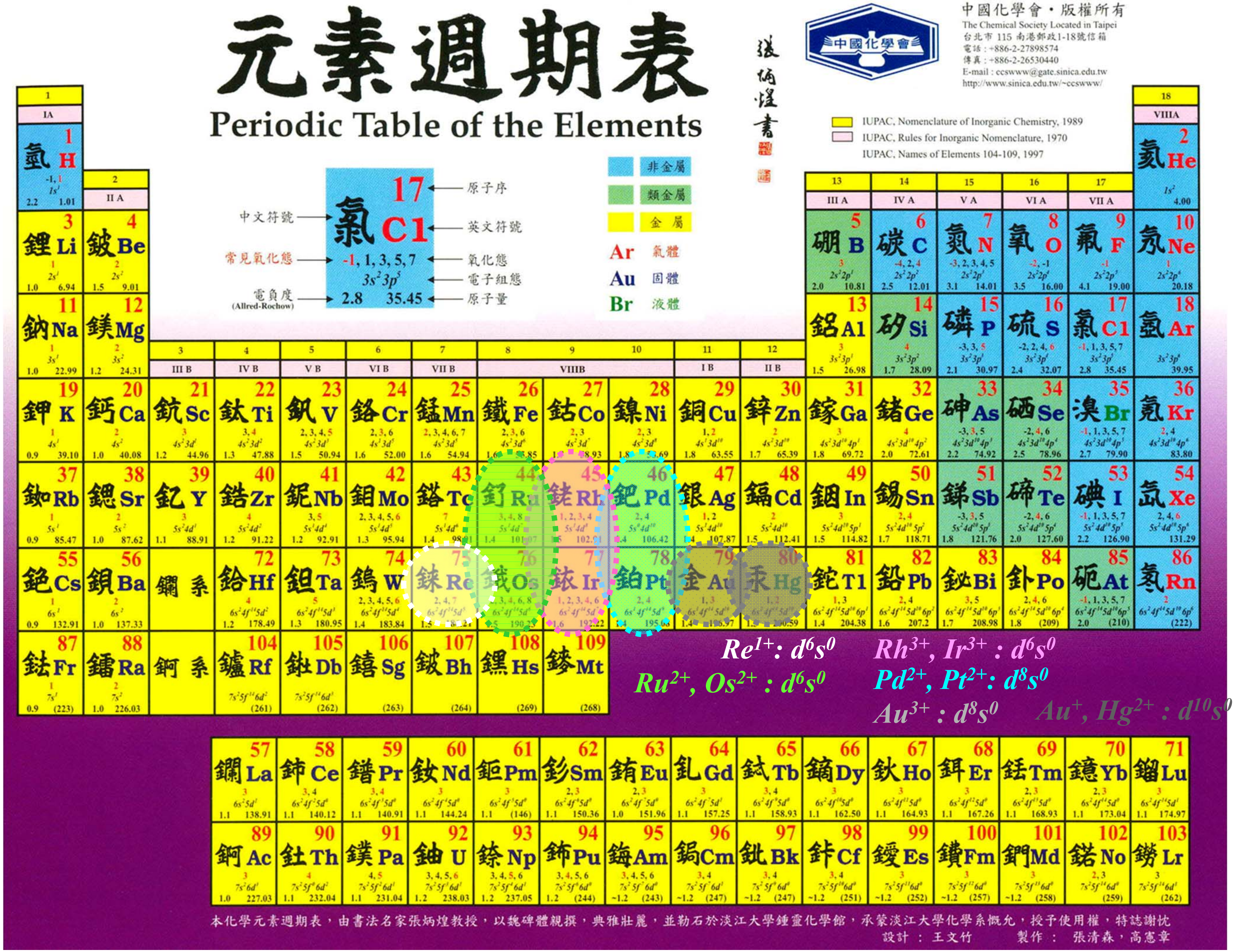
LI: low refractive index (n =1.51)
HI: high refrative index (n= 1.78)
HI-2: 205 nm TPBI
HI-3: 210 nm TPBI
HI: 40 nm TPBI



For a classical phosphorescence emitter, emission lifetime is too long, longer than the vibrational motion of the molecules. Therefore, most triplet state emission (phosphorescence) will be quenched due to the nonradiation decay process (vibration motion) and can not be observed at room temperature.

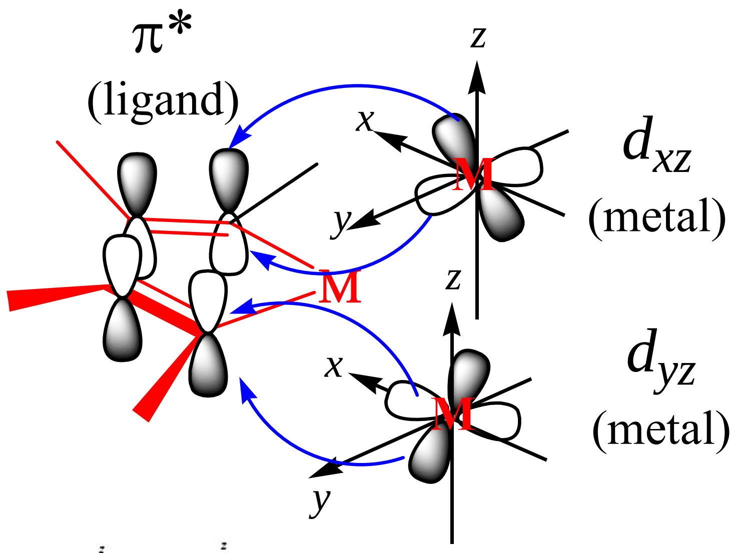


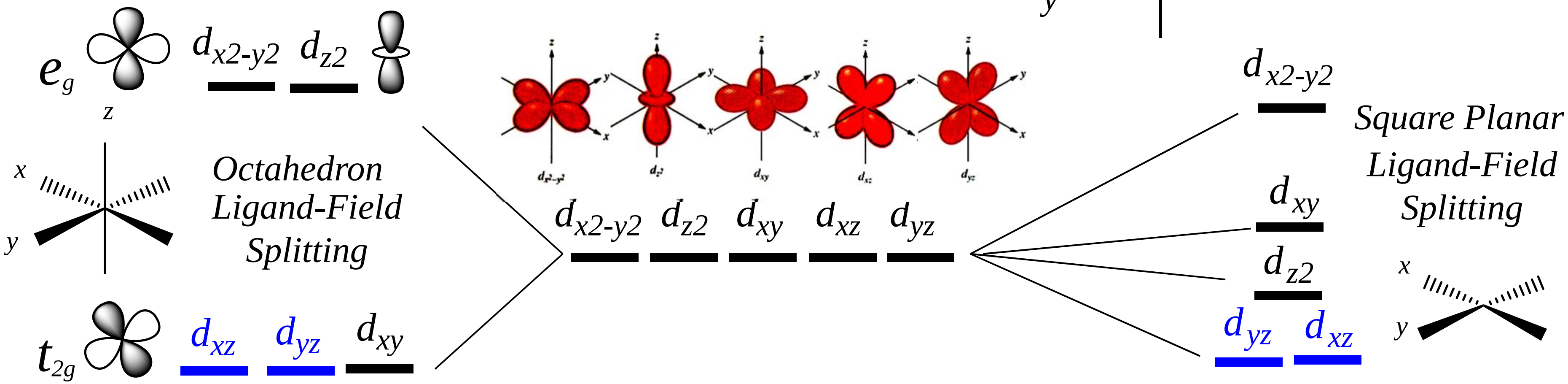
Forrest, S. R. at 2003 International Display Manufacturing Conference (IDMC).


元素週期表
Periodic Table of the Elements
張炳煌書
中國化學會・版權所有
The Chemical Society Located in Taipei
台北市 115 南港郵政1-18號信箱
電話：+886-2-27898574
傳真：+886-2-26530440
E-mail : ccswww@gate.sinica.edu.tw
http://www.sinica.edu.tw/~ccswww/
IUPAC, Nomenclature of Inorganic Chemistry, 1989
IUPAC, Rules for Inorganic Nomenclature, 1970
IUPAC, Names of Elements 104-109, 1997
非金屬
類金屬
金屬
Ar 氣體
Au 固體
Br 液體
原子序
中文符號
英文符號
常見氧化態
氧化態
電子組態
電負度 (Allred-Rochow)
原子量
Re^{1+}: d^6s^0
Rh^{3+}, Ir^{3+} : d^6s^0
Ru^{2+}, Os^{2+} : d^6s^0
Pd^{2+}, Pt^{2+}: d^8s^0
Au^{3+} : d^8s^0
Au^{+}, Hg^{2+} : $d^{10}s^0$
本化學元素週期表，由書法名家張炳煌教授，以魏碑體親撰，典雅壯麗，並勒石於淡江大學鍾靈化學館，承蒙淡江大學化學系概允，授予使用權，特誌謝忱
設計：王文竹 製作：張清森，高憲章

Metal to Ligand Charge Transfer (MLCT)

MLCT is the electronic interaction that realizes spin-orbital coupling in transition metal complexes and alleviates the forbiddance of $T_1 \rightarrow S_0$ i.e., phosphorescence of organic materials





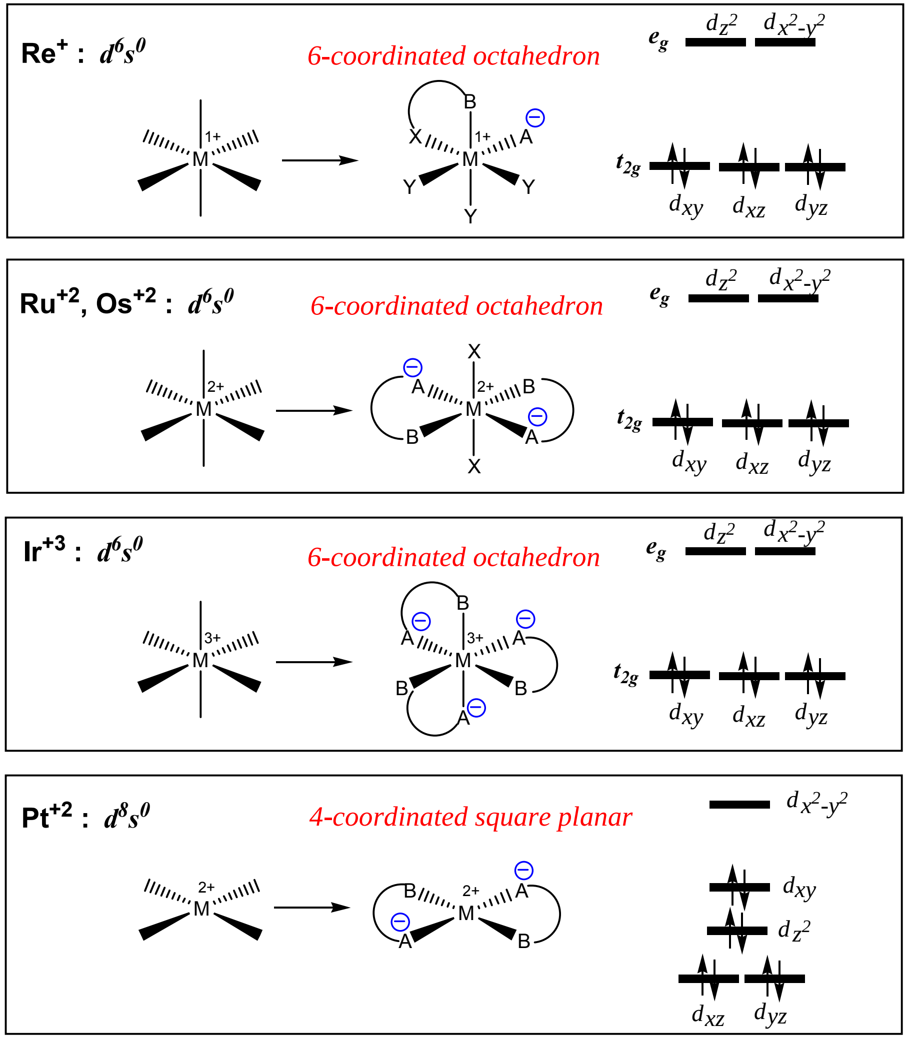
- Group B element has the number of electron ≤ 10 for five d-atomic orbitals
- Effective MLCT takes place only on transition metal (group B element) complexes because of availability of partially filled d-atomic orbitals for molecular valance bonding.

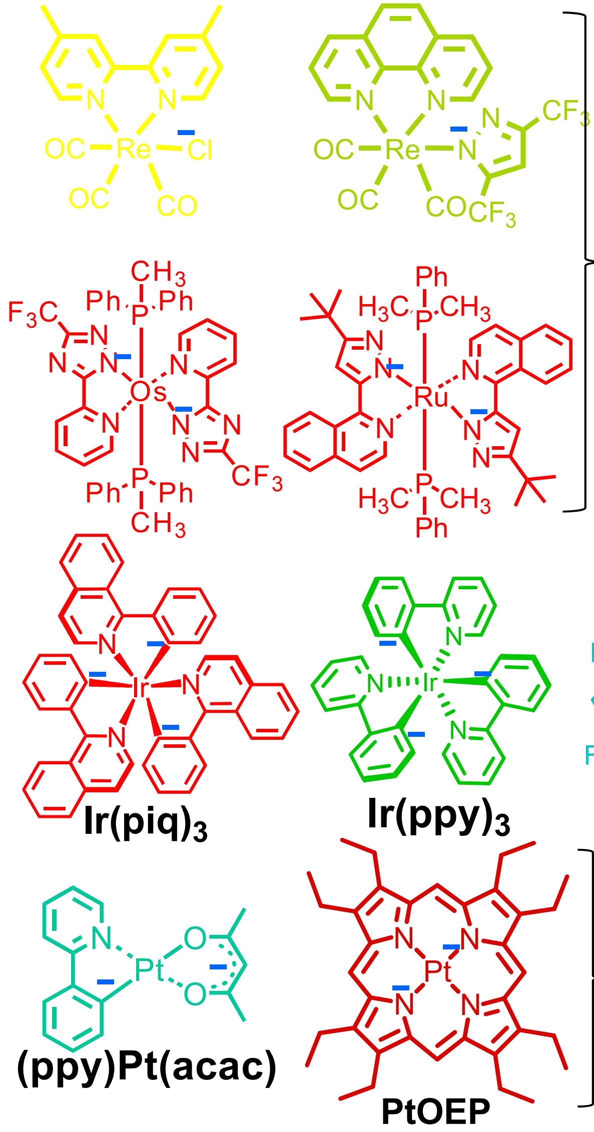
6-Coordinate Octahedron and 4-Coordinate Square Planar

(Re^{+}, Ru^{+2}, Os^{+2}, Ir^{+3}) (Pt^{+2})

Electronic configuration : No unpaired electron ⇨ **Zero net charge (Neutral transition metal complexes)**

⇨ **Facilitate vacuum-thermal-deposition process**





More difficult in finding appropriate ligand set for the neutralization of positive charge from metal cation

Rleability issue associated with blue phosphorescence

Square planar molecular shape is prone to π-π stacking, which enhances T_1-T_1 annihilation (emission quenching) and impairs to color purity (because of excimer emisssion)

Material Lifetime Status

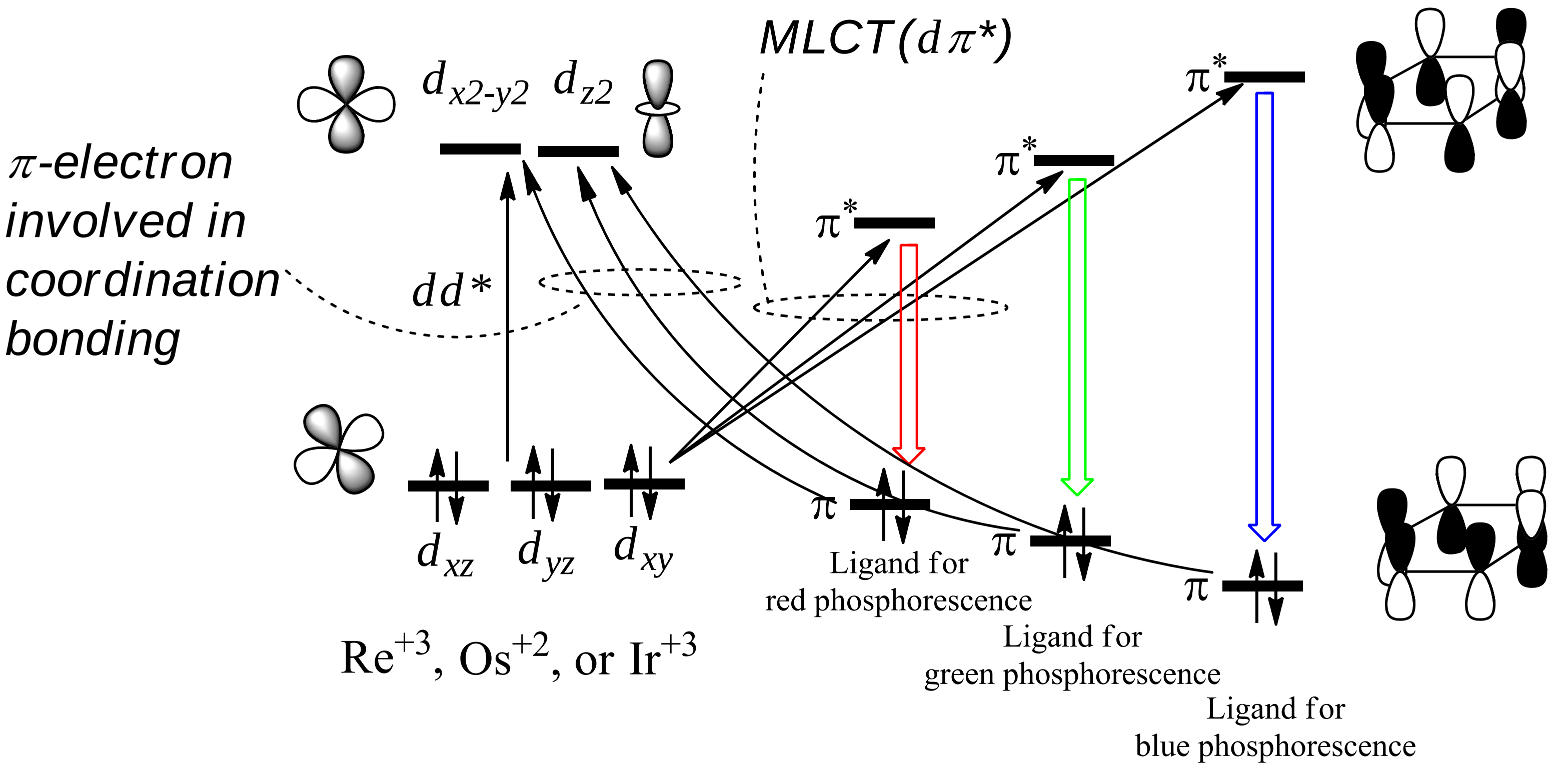
- ❑ Lifetime improvement by new materials very impressive.
- ❑ Relatively Blue lifetime is too short.

		Color	Efficiency (cd/A)	Lifetime	Company
Fluorescence	R	0.67, 0.33	11	>100,000h @1000cd/m²	Idemitsu, Mitsui Chem
	G	0.30, 0.63	25	>100,000h @1000cd/m²	Idemitsu
	B	0.15, 0.15 0.13, 0.22	7 9	>12,000h @1000cd/m² >23,000h @1000cd/m²	Idemitsu
Phosphorescence	R	0.65, 0.35 0.67, 0.33	20 12	>200,000h @500cd/m² >300,000h @500cd/m²	UDC
	G	0.28, 0.63	60	>40,000h @1000cd/m²	UDC
	B	0.16, 0.29	21	17,500h @200cd/m²	UDC
	B	*0.14, 0.15*	*9*	*10,000h@200cd/m²*	*UDC*
	B	*0.16, 0.10*	*3*	*under developement@200 cd/m²*	*UDC*

Reliability Problem

IMID/IDMC '06 Digest, 16-1, p. 305.
http://www.universaldisplay.com/pholed.htm
http://www.idemitsu.co.jp/denzai/el/index.html

Blue phosphorescence organic light-emitting material is not stable



⊿ *dd** Electronic transition is coordination bonding repulsive and it makes the coordination complexes photochemically unstable.

⊿ The high *π** energy level, such as that of blue phosphorescence ligand, facilitates *dd* electronic transition and photo-degradation of coordination complexes*

Chi, Y.; Chou, P.-T. *Chem. Soc. Rev.* **2010**, *39*, 638.

Chou, P.-T.; Chi, Y. et al. *Coord. Chem. Rev.* **2011**, *255*, 2653.

Chou, P.-T.; Chi, Y. et al. *Mater. Today* **2011**, *14*, 472

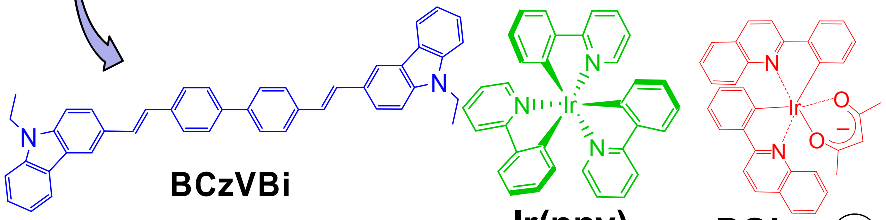
nature | Vol 440|13 April 2006| 908

Using stable fluorescence blue dopant instead of unstable phosphorescence blue dopant

Management of singlet and triplet excitons for efficient white organic light-emitting devices

Yiru Sun[1], Noel C. Giebink[1], Hiroshi Kanno[1], Biwu Ma[2], Mark E. Thompson[2] & Stephen R. Forrest[1]†

[1]Department of Electrical Engineering, Princeton Institute for the Science and Technology of Materials (PRISM), Princeton University, Princeton, New Jersey 08544, USA. [2]Department of Chemistry, University of Southern California, Los Angeles, California 90089, USA. †Present address: Department of Electrical Engineering and Computer Science, Department of Physics, and Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA.



1

Separate channels for triplet (T) and singlet (S) formation and transfer

3 *Diffusion of singlet excitons to the phosphor dopants is negligible due to their intrinsically short diffusion lengths*

EL efficiency is compromised

With lamp lighting fixture

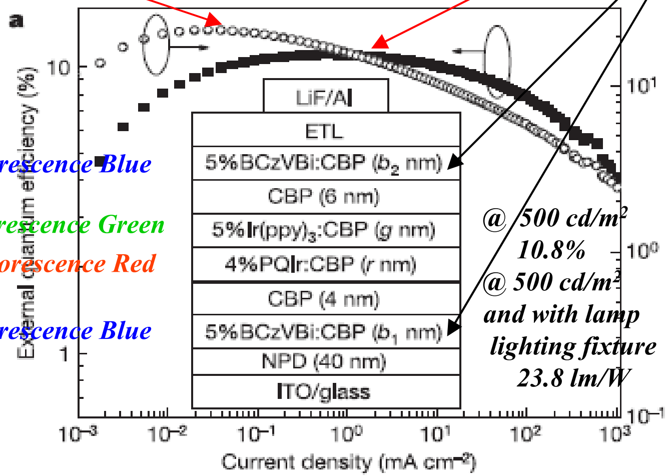
22 lm/W (37.6 lm/W) *11% (18.7%)*

Fluorescence Blue

Phosphorescence Green

Phosphorescence Red

Fluorescence Blue



@ 500 cd/m² 10.8%

@ 500 cd/m² and with lamp lighting fixture 23.8 lm/W

Majority of exciton, either S or T, is formed at each side of phosphorescence dopant layer

1.7 mA/cm²

6.8 mA/cm²

28 mA/cm²

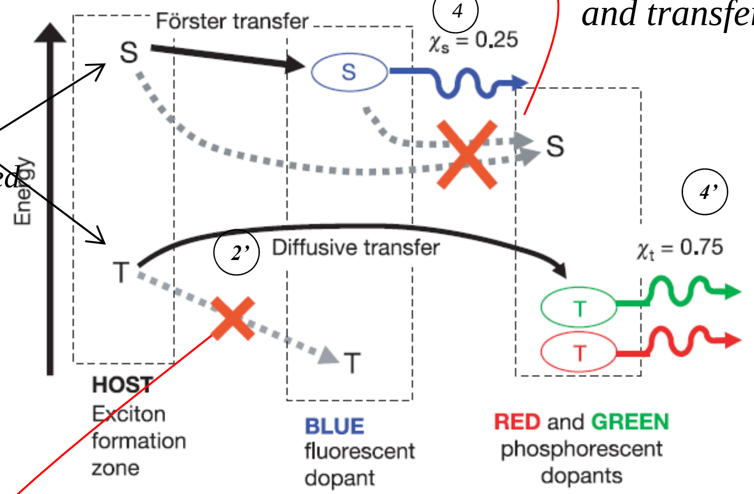


Figure 1 | Proposed energy transfer mechanisms in the fluorescent/phosphorescent WOLED. This illustrates the separate channels for triplet

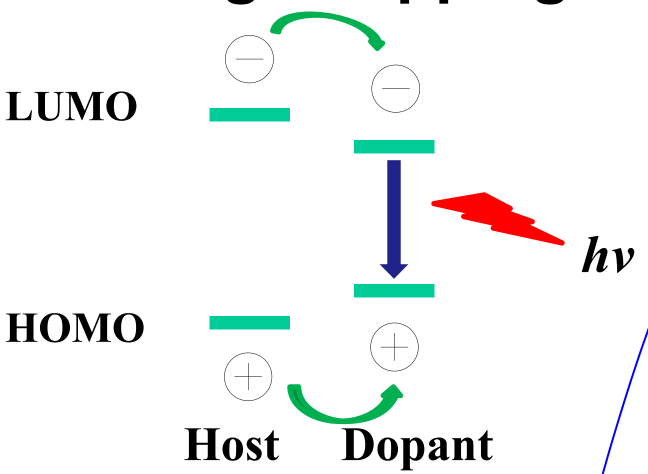
2 *The non-radiative host triplets, however, cannot efficiently transfer to the fluorophore by the Förster mechanism, or by Dexter transfer owing to the low doping concentration (5%)*

Reduced sensitivity of η_{ext} to current density (efficiency roll-off) is another clear difference between the WOLED of this study and previous (all-phosphor WOLED).

This approach has the further advantages of a stable white balance with current, a high efficiency at high brightness due to reduced geminate exciton recombination, and an enhanced lifetime due to the combined use of a stable fluorescent blue, and long lived phosphorescent green and red, dopants in a single emissive region.

Occurrence of Exciton on Dopants

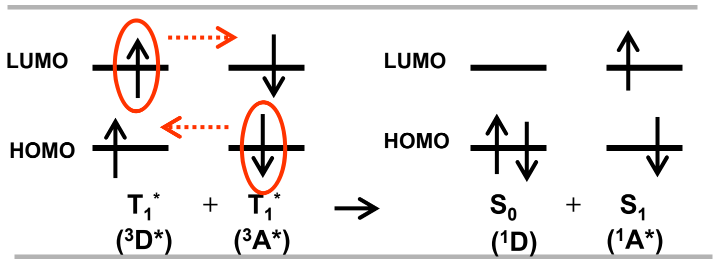
1. Charge trapping



Triplet-triplet energy transfer is hardly observed for organic material, because there is hardly any organic material having ground state electron in triplet configuration.

- ***Major quenching mechanism of phosphorescence material***

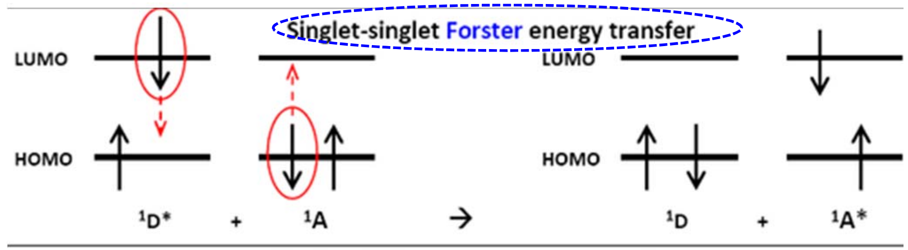
Triplet-triplet annihilation (TTA)



2. Energy transfer

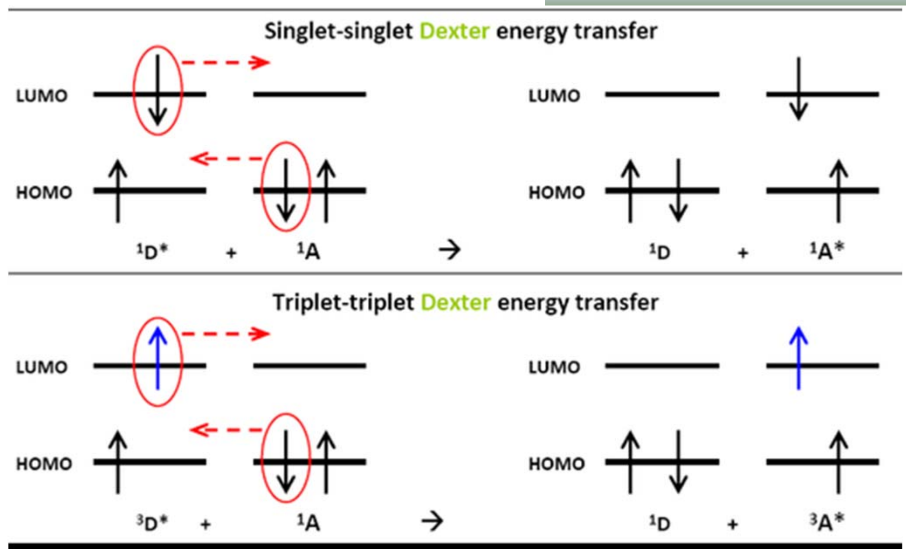
- ***Förster energy transfer***

dipole-dipole coupling:
fast process (~10-12 sec)
long distant process (up to 100 A)



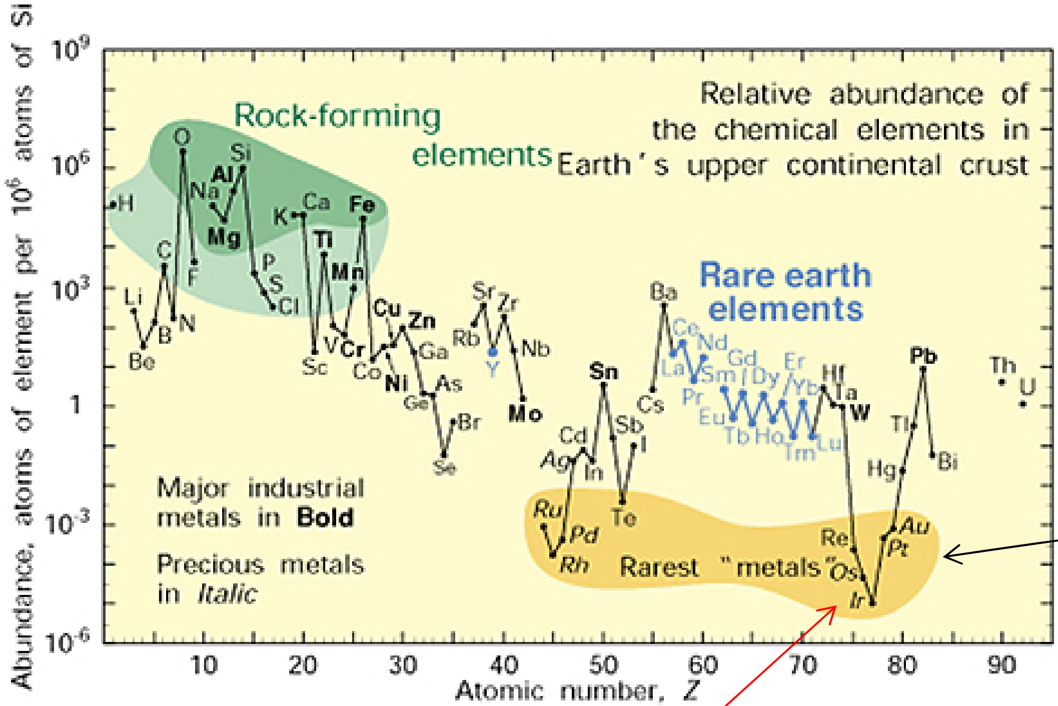
- ***Dexter energy transfer***

require electron exchange
short distant process (15-20 A)



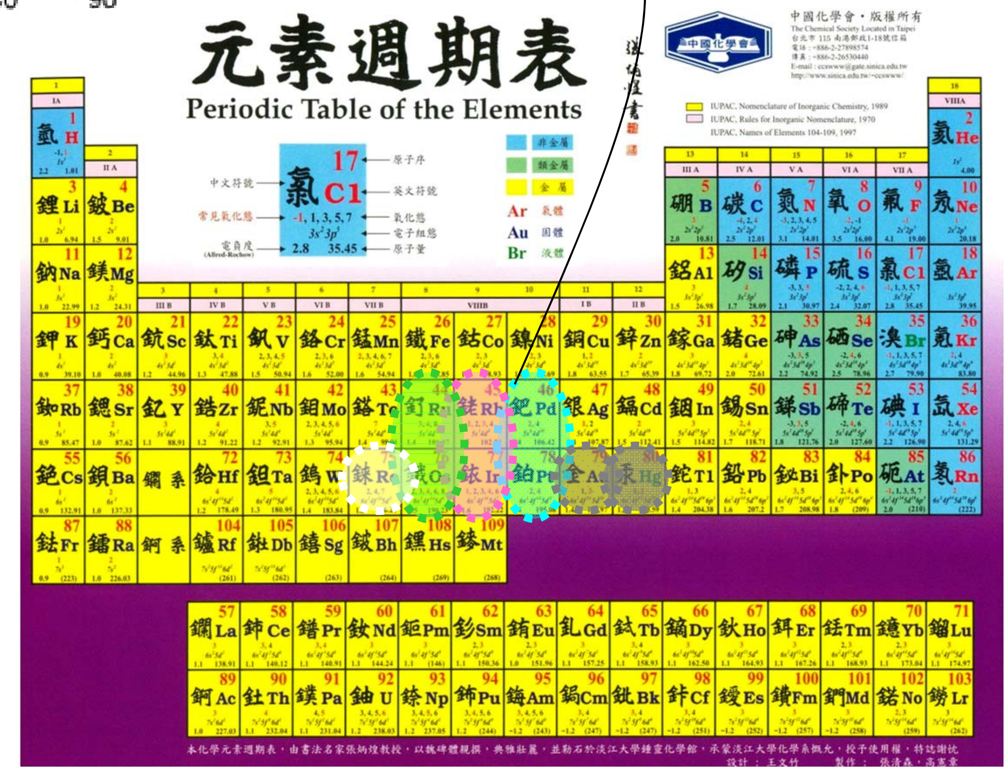
Exciton hops from donor to acceptor

http://chemwiki.ucdavis.edu/Theoretical_Chemistry/Fundamentals/Dexter_Energy_Transfer#Introduction



Rarest "metals"

最稀有的"金屬"



Ir is the rarest of the rarestest!

Ir (銥)名列最稀有金屬裡的最稀有!

⇩

昂貴!

Expensive!

Highly efficient organic light-emitting diodes from delayed fluorescence

Hiroki Uoyama[1], Kenichi Goushi[1,2], Katsuyuki Shizu[1], Hiroko Nomura[1] & Chihaya Adachi[1,2]

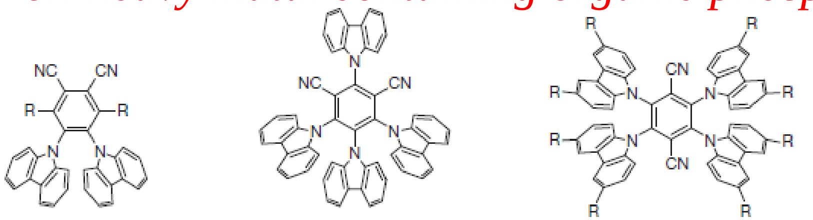
[1]Center for Organic Photonics and Electronics Research, Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan. [2]International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan.

THE 3RD GENERATION OLED MATERIALS

"Thermally activated delayed fluorescence (TADF)"

"Non-heavy matal containing organic phosphorescence materials"

b



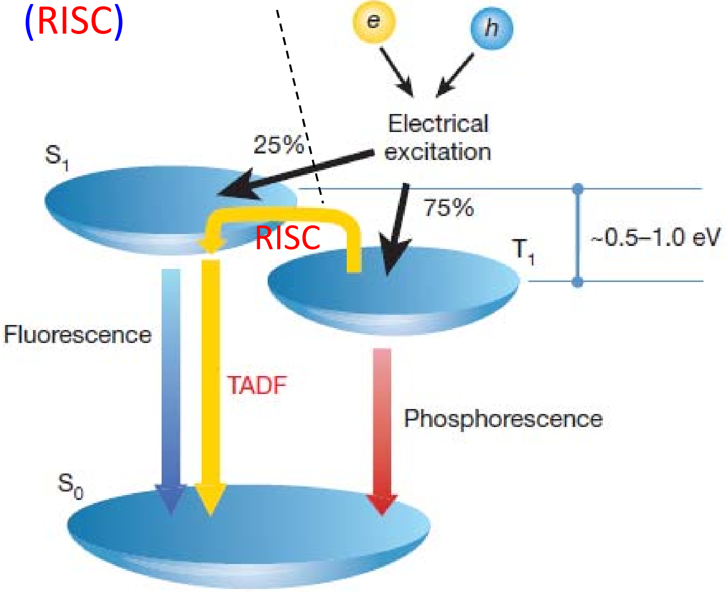
4CzPN: R = carbazolyl
2CzPN: R = H

4CzIPN

4CzTPN: R = H
4CzTPN-Me: R = Me
4CzTPN-Ph: R = Ph

- Small ΔE_{ST} (< 0.2 eV) is necessary for reverse intersystem crossing (RISC)

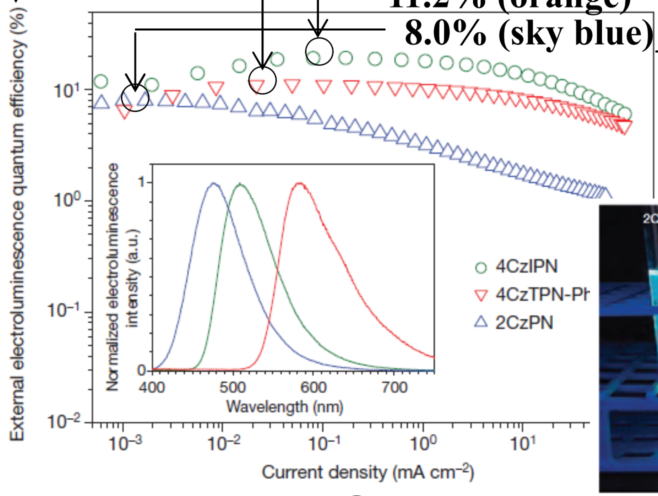
Room Temp (25 °C) kT
= 0.593 Kcal mol^{-1}
= 0.0257 eV

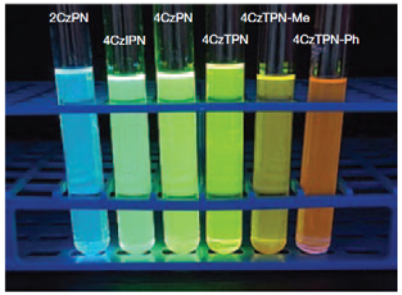


EQE (η_{EXT}) of OLED

"All surpass EQE~5%, the upper limit for organic fluorescence materials "

19.3% (green)
11.2% (orange)
8.0% (sky blue)





For green and orange OLEDs:

ITO/NPB(35 nm)/CBP:4CzIPN or 4CzTPN-Ph (5 wt%, 15 nm)/ TPBi (65 nm)/LiF (0.8 nm)/Al (70 nm)

For sky blue OLED:

ITO/NPB(40 nm)/mCP (10 nm)/PPT:2CzPN (5 wt%, 20 nm)/ PPT (40 nm)//LiF (0.8 nm)/Al (70 nm)

Molecular structure design for small ΔE_{ST} and hence TADF

- Principle of Small ΔE_{ST} $\Rightarrow$ Small spatial overlap between HOMO and LUMO

Singlet band-gap energy

Coulomb interaction integral

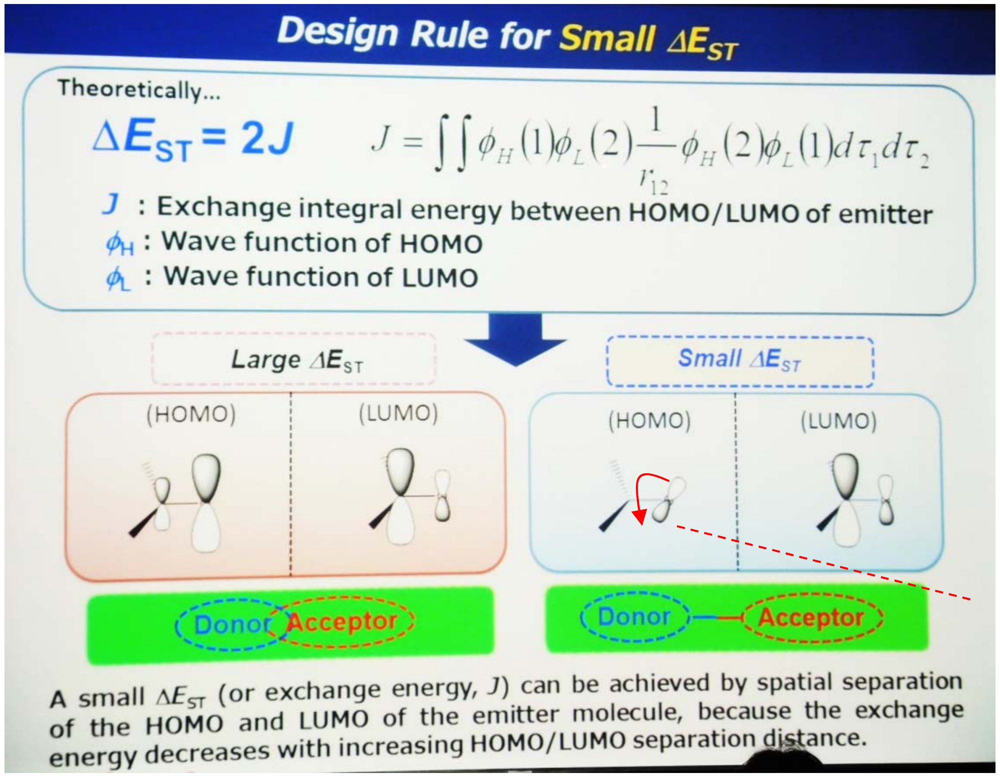
Singlet-triplet splitting (energy difference)

$$\left.\begin{aligned} \Delta E_S &= E_{gap} - J + 2K \\ \Delta E_T &= E_{gap} - J \end{aligned}\right\} \Delta E_{ST} = \Delta E_S - \Delta E_T = 2K$$ (Exchange interaction integral)

Triplet band-gap energy

$$2K \propto \int \psi_{HOMO}(r)\,\psi_{LUMO}(r)\,d^3r$$

M. Klessinger and J. Michl *Excited States and Photochemistry of Organic Molecules*, VCH Publishers, New York 1995.

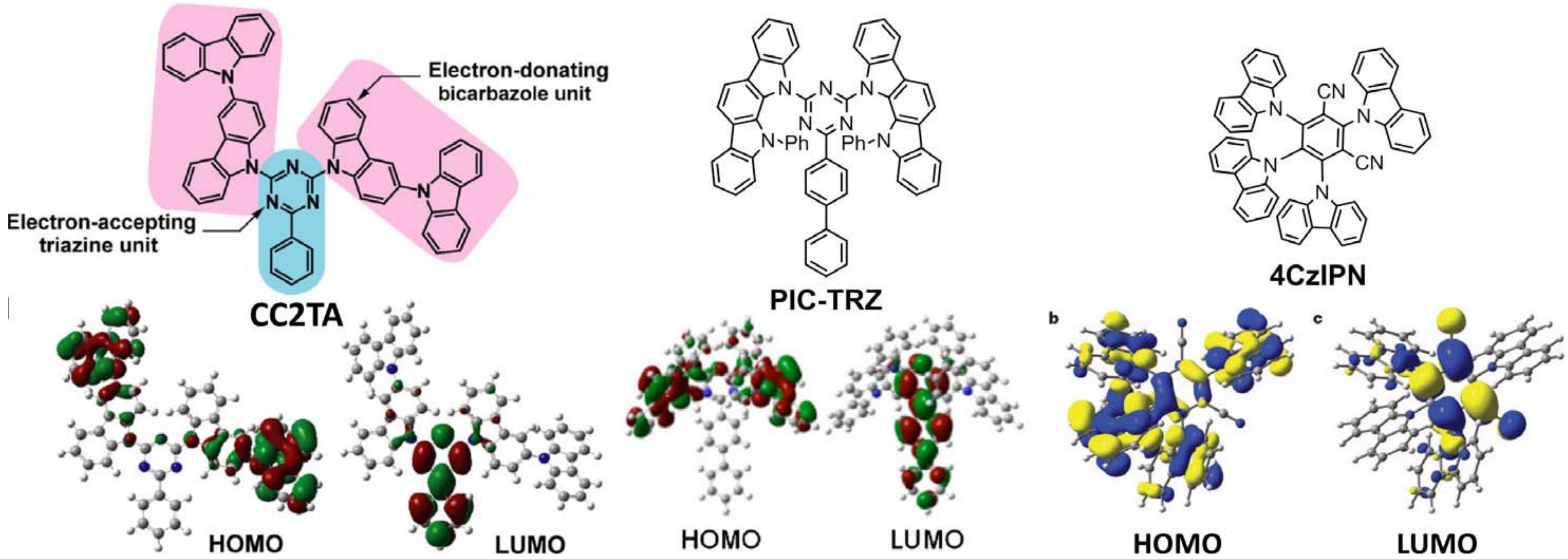


Picture taken from the lecture by Chihaya Adachi in ISNA-15 (15th International Symposium on Novel Aromatic Compounds) 2013, Taipei, Taiwan.

Twisted or non π-conjugated !

Three TADF OLEDs

A limited spatial overlapping between ψ_{HOMO} and ψ_{LOMO} $\Rightarrow$ small ΔE_{ST} (~0.1 eV)



Relatively low solution PL quantum yield $\Rightarrow$

	CC2TA	PIC-TRZ	4CzIPN
$E(S_1)$	2.91 eV	2.66 eV	2.38 eV
$E(T_1)$	2.85 eV	2.55 eV	2.30 eV
ΔE_{ST}	0.06 eV	0.11 eV	0.08 eV
ϕ_{PL}	~45%	35~39%	~94% ???
EQE_{max}	~11%	~5.3%	~19.3%
λ_{max}^{EL}	490 nm	495 nm	510 nm

CC2TA: Lee, S. Y.; Yasuda, T.; Nomura, H.; Adachi, C. *Appl. Phys. Lett*. **2012**, *101*, 093306.
PIC-TRZ: Endo, A.; Sato, K.; Yoshimura, K.; Kai, T.; Kawada, A.; Miyazaki, H.; Adachi, C. Appl. Phys. Lett. **2011**, 98, 083302
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NATURE PHOTONICS | VOL 8 | APRIL 2014 | 326

ARTICLES
PUBLISHED ONLINE: 2 MARCH 2014 | DOI: 10.1038/NPHOTON.2014.12

nature photonics

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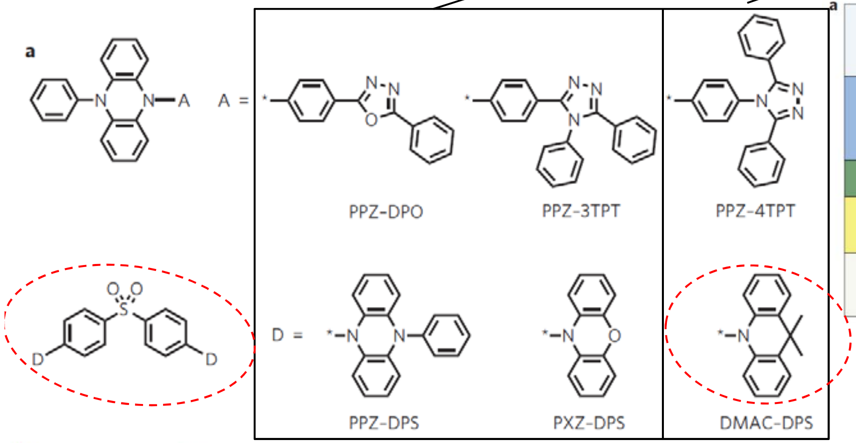
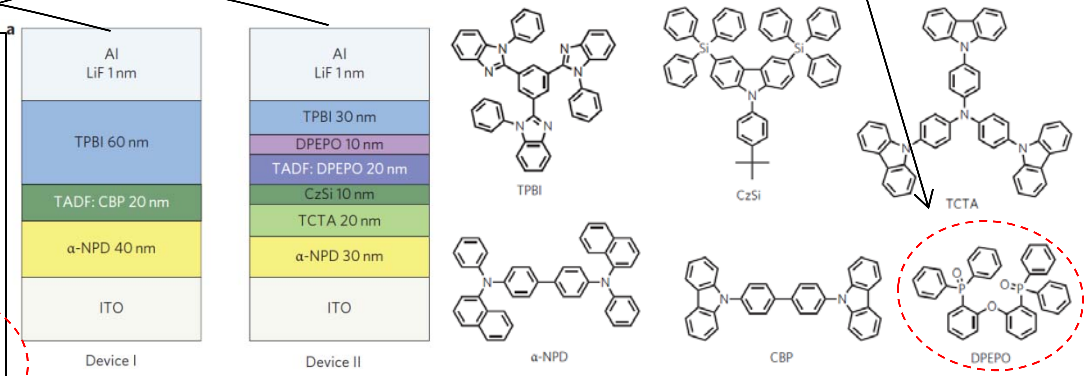
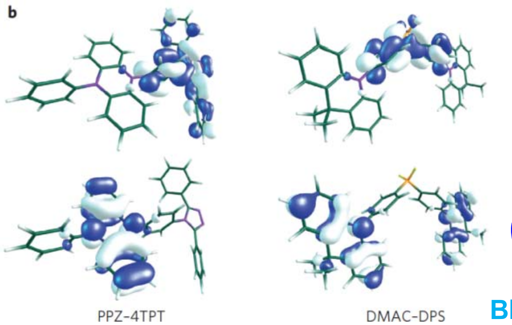
Efficient blue organic light-emitting diodes employing thermally activated delayed fluorescence

Qisheng Zhang[1†], Bo Li[1†], Shuping Huang[1], Hiroko Nomura[1], Hiroyuki Tanaka[1] and Chihaya Adachi[1,2*]

Host Material T_1: 3.30 eV



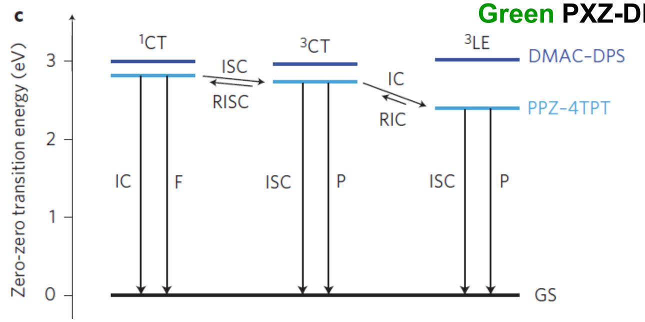


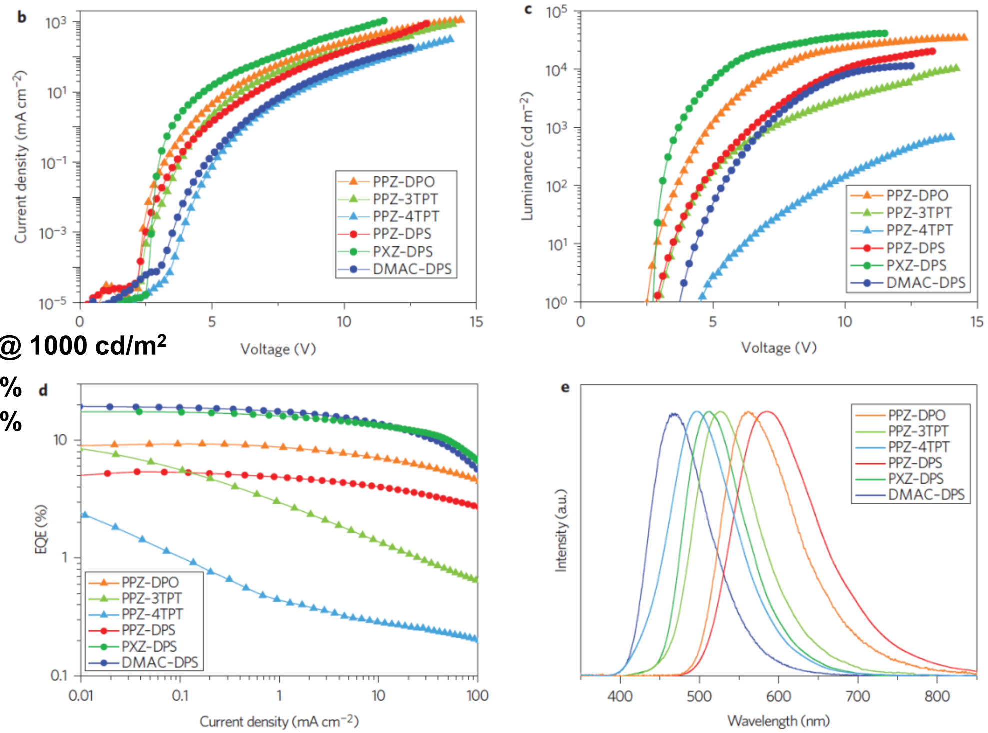


True Blue!

CIE$_{x,y}$ (0.16,0.20)

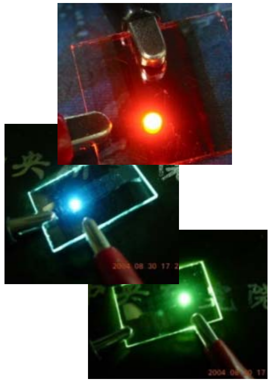
	EQE$_{max}$	EQE @ 1000 cd/m^2
Blue DMAC-DPS	19.5%	15.5%
Green PXZ-DPS	17.5%	16.0%





SUMMARY

OLED flat panel display



√

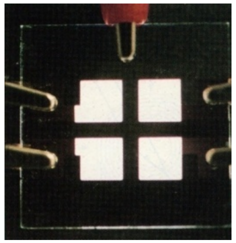
Samsung Galaxy Series

31 in. full-HD AMOLED prototype TV by LG Display, 2010

2013

In 2014, LG drops the price of 55" OLED TV to 3750 USD (it was ~10,000 USD in 2013)

White OLED lighting or illumination



Junji Kido
Yamagata Univ.
1995

√ Efficiency

√? Lifetime

√? Cost

TADF materials

Chihaya Adachi
Kyushu Univ.
2012

DVICE, NBC Universal, GE

Lumiotec.com

Siemens.com

Philips Mirrorwall

Novaled AG

Osram.com

GE Konica Minolta