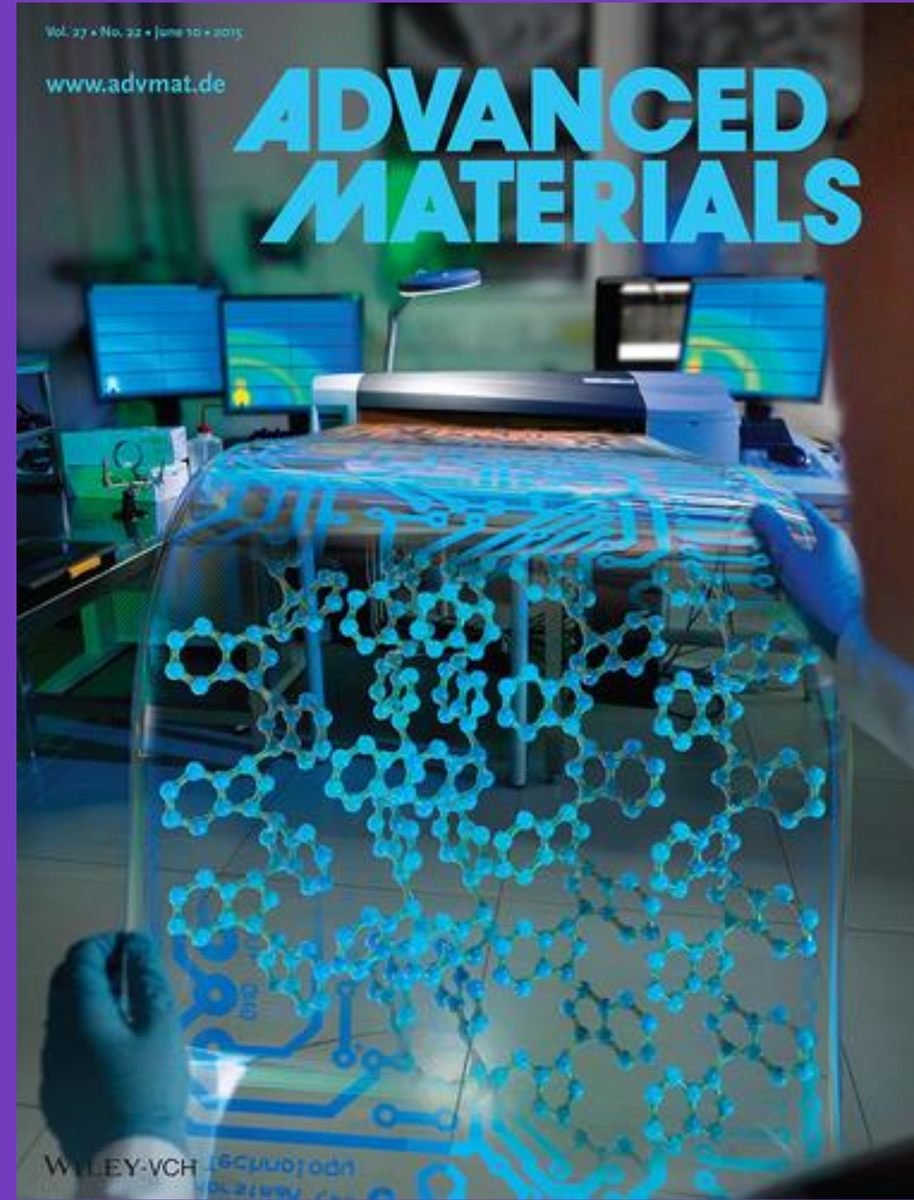
ELEC-E9210 Organic Electronics: Materials, Devices & Applications

Organic Light Emitting Diode I

Aalto University
School of Electrical Engineering

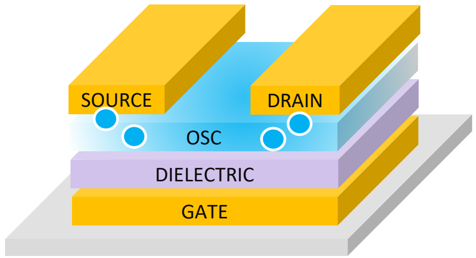
https://organicelectronics.aalto.fi



Today´s Class

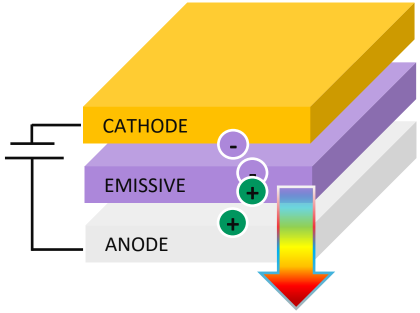
Previously…

- **Organic field effect transistors**: basic **principles** and **charge transport** mechanism
- **Building blocks** of OFET
- **Applications** of **OFET** in several fields



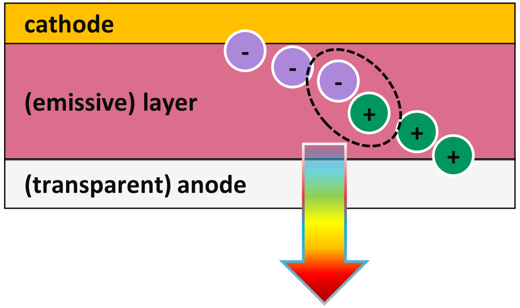
Today

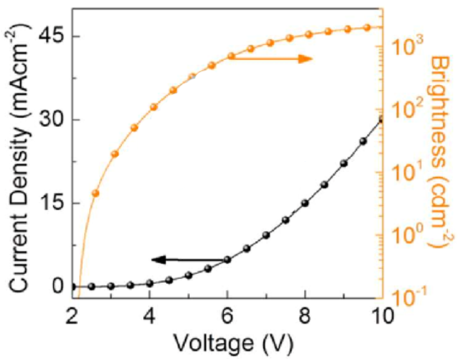
- **Organic Light Emitting Diode** (OLED): fundamental characteristics, functioning and materials
- **Applications** of **OLEDs**



Organic Light Emitting Diode (OLED)

Organic Light Emitting Diodes are diodes made of organic materials capable of ***generating light*** when ***biased in the forward direction***.

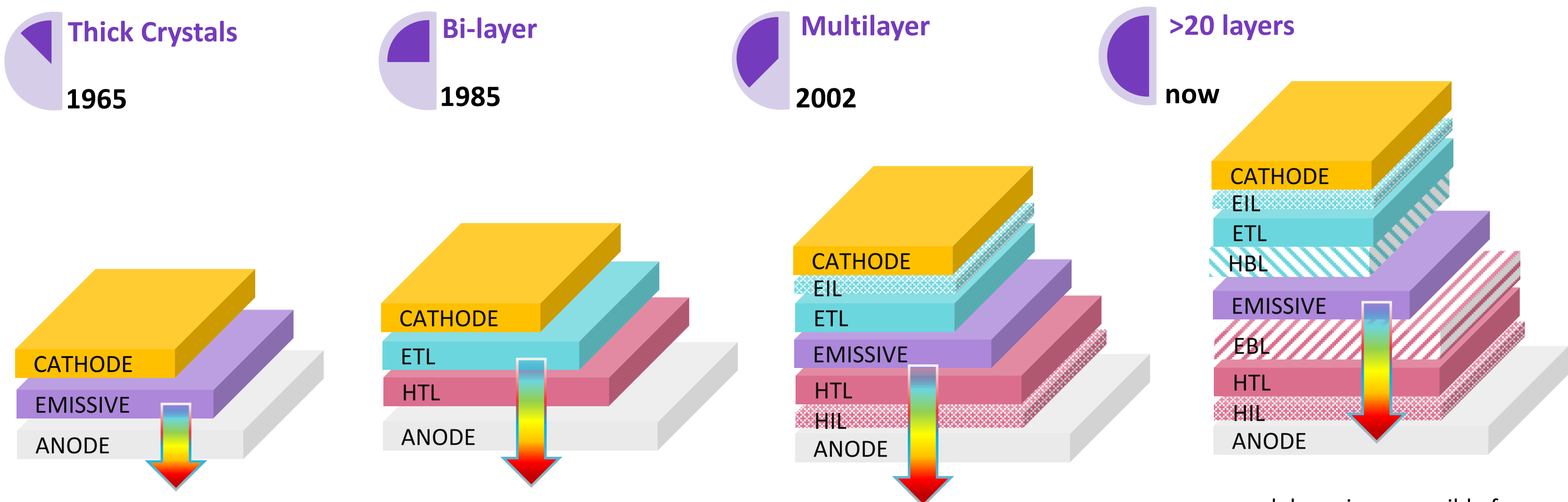




ACS Appl. Mater. Int. **9**(3), 2711 (2017)

Upon bias, holes (electrons) are injected from anode (cathode) and then transported into the electroluminescent layer, where they form an exciton which can then decay radiatively

OLED: A 45 Years Old Journey



single ***ambipolar emissive*** layer

p/n junction

each layer is responsible for enhancing ***injection/transport***

each layer is responsible for enhancing ***injection/transport*** and ***blocking*** the other one

(E)HTL: (electron) hole ***transporting*** layer
(E)HIL: (electron) hole ***injection*** layer
(E)HBL: (electron) hole ***blocking*** layer

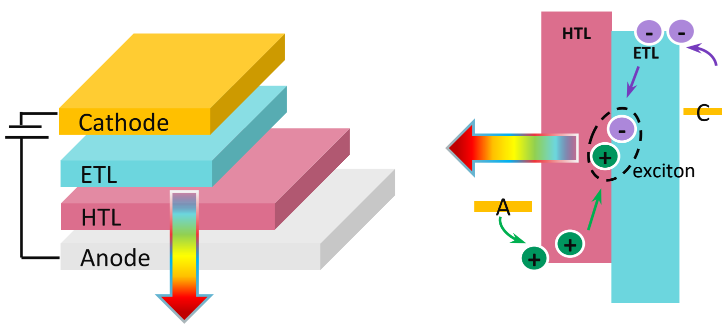
increasing complexity leads to improved efficiency

Further Reading: Polym. Int. **55**, 572 (2006)

OLED: *pn Junction*

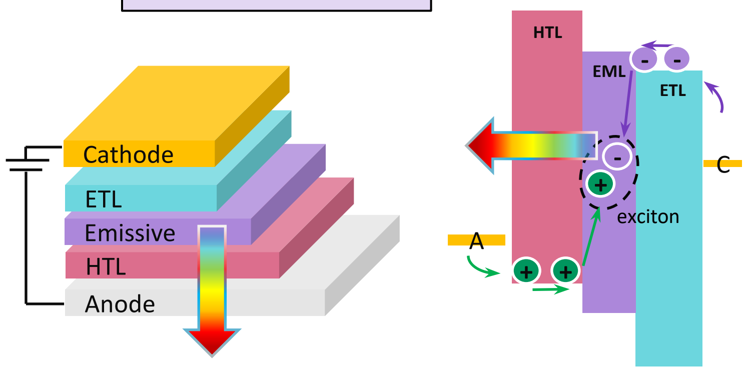
An efficient OLED device requires h^+/e^- transport to be balanced
(efficient excitons formation and decay)

p-n junction



Excitons form at the interface (ETL/HTL)

Multi-layer structure

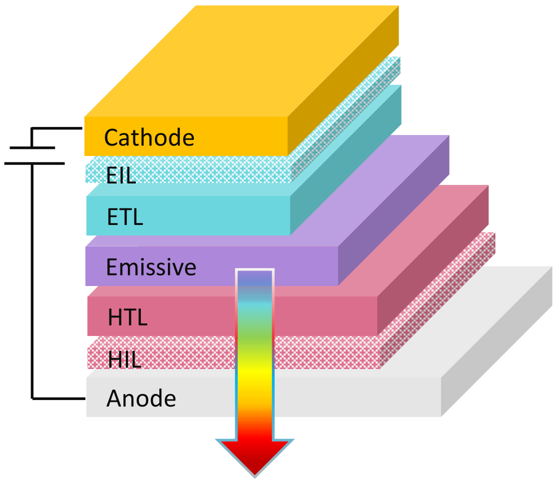


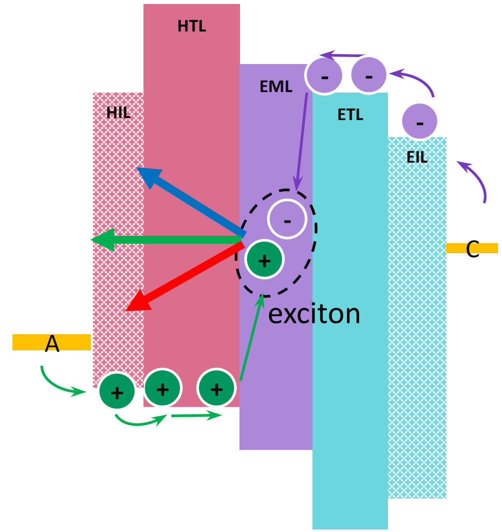
Excitons form in the emissive layer (EML), with charges coming through the transport layers (ETL/HTL)

OLED: *Multilayer Structure*

Highly efficient OLED includes a multilayer structures, where each layer is optimized for a specific function

- carrier injection
- carrier transport
- *e-h* recombination/exciton formation
- radiative/non-radiative recombination





OLED: Photometric Parameters

$$\textbf{External Quantum Efficiency}, \eta_{ext} = \frac{\#\ of\ emitted\ photons}{\#\ of\ injected\ charges} = \eta_r\, \phi_f\, \chi\, \eta_{out}$$

- η_r: *e-h* recombination probability (can approach 1)
- ϕ_f: fluorescent quantum efficiency (can approach 1)
- χ: radiative decay probability (<25%)
- η_{out}: fraction of photons escaping the device (~20%)

classical OLED
~4-5%

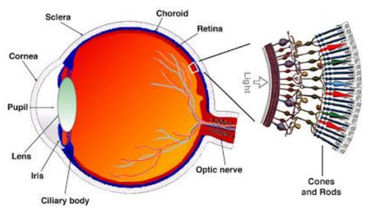
$$\textbf{Luminance} = \frac{amount\ of\ emitted\ light}{device\ area}\ [\boldsymbol{Cd}]$$

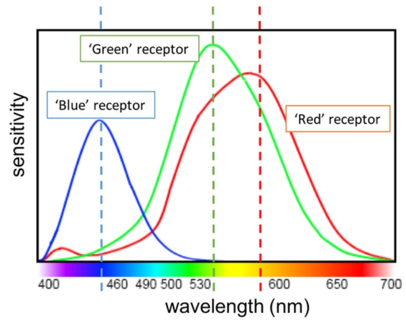
$$\textbf{Current Efficiency}, \eta_L = \frac{luminance}{\#\ of\ injected\ charges} = \frac{L}{J}\left[\frac{Cd/m^2}{A/m^2}\right] = \frac{L}{J}\left[\frac{Cd}{A}\right]$$

$$\textbf{Luminous Efficiency}, \eta_P = \frac{total\ luminous\ flux}{total\ radian\ flux} = \frac{L}{J}\frac{\pi}{V} = \eta_L\frac{\pi}{V}\ \left[\frac{Cd}{A}\frac{rad}{V} = \frac{lm}{W}\right]$$

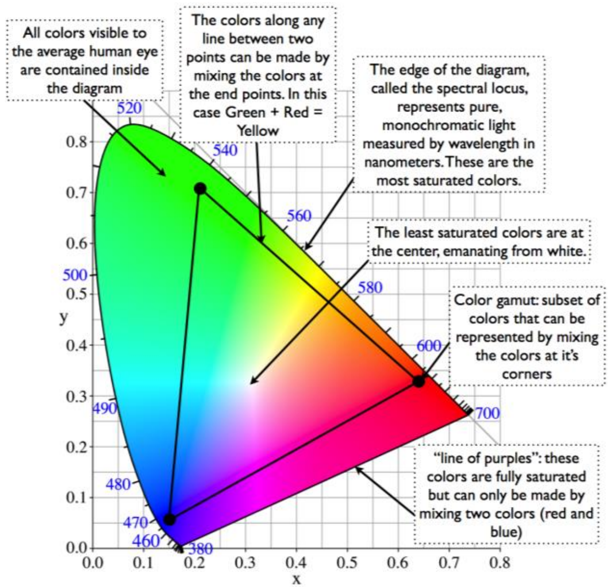
OLED Color Perception & Color Map (CIE)

Human eye is sensitive to fundamental color differently





Sensitivity of the human eye to light varies strongly over the wavelength range 380-800nm. Under daylight conditions, the average normal sighted human eye is most sensitive at a wavelength of 555 nm (green light at this wavelength produces the impression of highest "brightness“)



CIE: Commission Internationale d'Eclairage (CIE)

CIE map characterizes colors by a luminance parameter Y and two color coordinates (x, y) which specify the point on the chromaticity diagram. ***All colors visible to the average human eye are contained inside the diagram***.

OLED Materials: Anode & Cathode

Work-function (ϕ) of the injecting electrodes has to match the HOMO or LUMO level of the transport layer

Low Work Function Metals		
metal	Φ (eV)	electrode
ITO	4.6	A
Al	4.28	C
Ag	4.26	C
In	4.12	C
Mg	3.66	C
Ca	2.87	C
Li	2.90	C
Cs	2.14	C

light extraction from bottom electrode

anode, usually a high work-function ***transparent*** conductive materials (ITO is very commonly used)

cathode, usually a thin film of metal with low work-function, allowing for an efficient *e*-injection onto the OSC LUMO.

- if cathode is thin enough (~10nm), light can be extracted also from cathode→ ***both top*** and ***bottom emission***

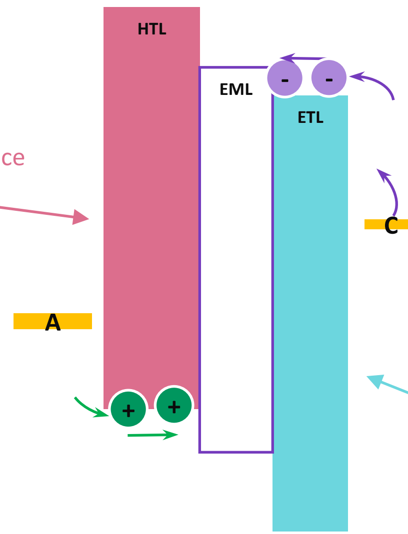
OLED Materials: Transport (Blocking) Layer(s)

The hole (electron) transporting layer has a two-fold purpose:

(a) ***hole (electron) transport*** layer

(b) ***blocking*** layer to confine electrons (holes) in the emissive layer (can be engineered)

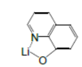
- ***pinhole free*** glassy film (film uniformity)
- ***low ionization potential*** for efficient injection
- ***high glass transition temperature*** (critical for device operation)
- ***wide optical bandgaps*** (small LUMO)



LT-E301 | Liq

8-Hydroxyquinolinolato-lithium

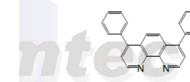
CAS No. : 850918-68-2
Grade : Sublimed, > 99.5% (HPLC)
Formula : C_9H_6NOLi
M.W. : 151.09 g/mole
UV : 261 nm (in THF)
PL : 514 nm (in THF)
TGA : > 350 °C (0.5% weight loss)



LT-E305 | Bphen

4,7-Diphenyl-1,10-phenanthroline

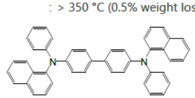
CAS No. : 1662-01-7
Grade : Sublimed, > 99.5%
Formula : $C_{24}H_{16}N_2$
M.W. : 332.4 g/mole
UV : 272 nm (in THF)
PL : 379 nm (in THF)
TGA : > 240 °C (0.5% weight loss)



LT-E101 | NPB

N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine

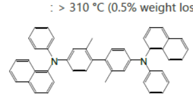
CAS No. : 123847-85-8
Grade : Sublimed, > 99.5% (HPLC)
Formula : $C_{44}H_{32}N_2$
M.W. : 588.74 g/mole
UV : 339 nm (in THF)
PL : 450 nm (in THF)
TGA : > 350 °C (0.5% weight loss)



LT-E115 | α-NPD

N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-2,2'-dimethylbenzidine

CAS No. : 495416-60-9
Grade : Sublimed, > 99% (HPLC)
Formula : $C_{46}H_{36}N_2$
M.W. : 616.79 g/mole
UV : 307 nm (in THF)
PL : 447 nm (in THF)
TGA : > 310 °C (0.5% weight loss)



- ***pinhole free*** glassy film (film uniformity)
- ***high electron affinity*** (for efficient cathode injection)
- ***high glass transition temperature*** (critical for device operation)
- ***wide optical bandgaps*** (deep HOMO)

materials from http://www.lumtec.com.tw/

OLED Materials: Injection Layer(s)

Matching the work function of the injection electrode and the HOMO or LUMO level of the transport layer is quite challenging (energy barrier ~1eV)

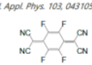
→ insert an ***extra layer to improve injection*** (lower the energy barrier)

LT-E208 | F4-TCNQ

2,3,5,6-Tetrafluoro-7,7,8,8-tetracyano-quinodimethane

CAS No.	: 29261-33-4
Grade	: Sublimed, > 99%
Formula	: $C_{12}F_4N_4$
M.W.	: 276.15 g/mole
UV	: 339 nm (in THF)
PL	: 402 nm (in THF)
TGA	: > 210 °C (0.5% weight loss)

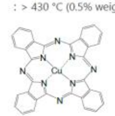
Reference : J. Appl. Phys. 103, 043105(2008)

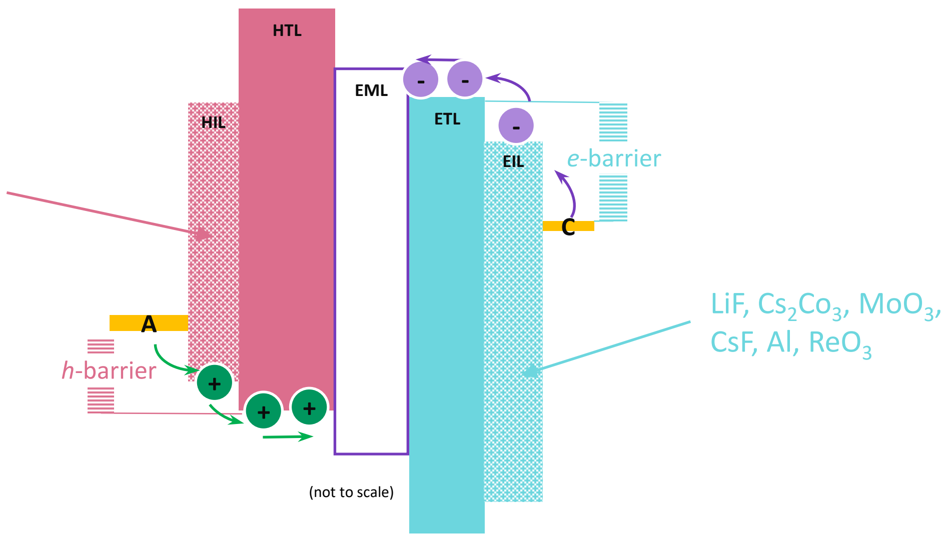


LT-E201 | CuPC

Copper(II) phthalocyanine

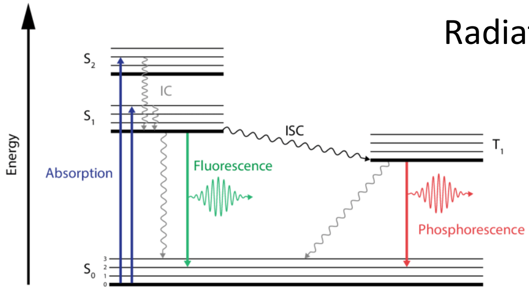
CAS No.	: 147-14-8
Grade	: Sublimed, > 99%
Formula	: $C_{32}H_{16}N_8Cu$
M.W.	: 576.07 g/mole
UV	: 345, 631 nm (in CH_2Cl_2)
PL	: 404 nm (film)
TGA	: > 430 °C (0.5% weight loss)





materials from http://www.lumtec.com.tw/

OLED Materials: Emissive Layer (I)

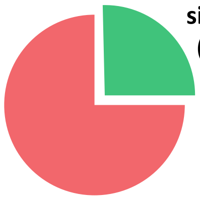


Radiative decay can occur through fluorescence and phosphorescence, depending on the spin of the excited state

FLUORESCENCE: electron in **excited state (<u>singlet</u>)** decays to a **lower energy state** (τ ~10^{-9}-10^{-7}s)

PHOSPHORESCENCE: electron in **excited state (<u>triplet</u>)** decays to a **lower energy state** (τ ~10^{-4}-10^{-1}s)

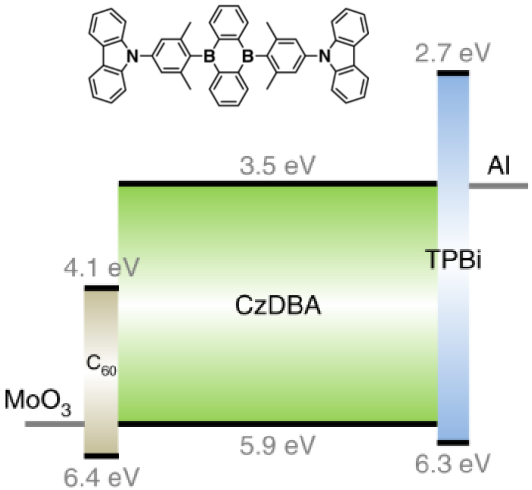
according to spin statistics

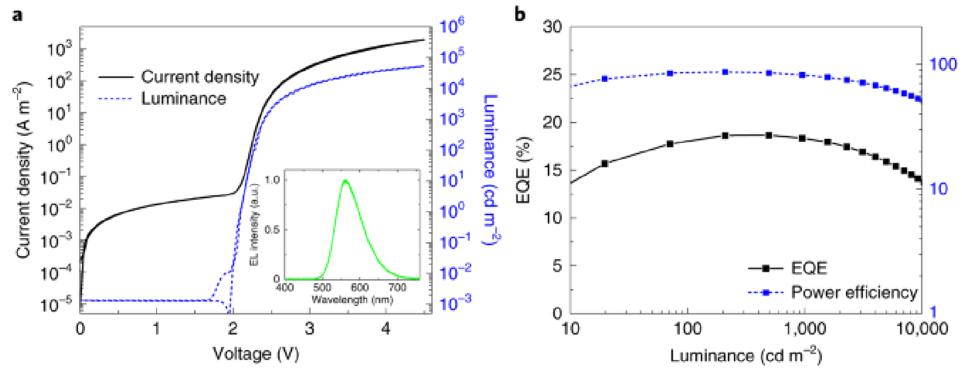


- most phosphorescent molecules show high phosphorescence only at very low-T
- few rare earth organic complexes (Y, lanthanides) show high phosphorescent quantum yield @RT

- *triplet states are <u>not radiative</u>*, thus the ***maximum fluorescent efficiency*** of an organic molecule is ***about 25%.***
- in the presence of ***heavy atoms***, singlet and triplet can form a mixed states due to strong *spin-orbit interaction* between the heavy atom and its ligand. Thus, singlet and triplet states can emit, in principle reaching a ***100% efficiency***.
- (many) isolated organic dye molecules exhibit very high fluorescence quantum yields (in solution) but in condensed phase, aggregation drastically reduces QY

OLED Emissive Layer: Single Layer





Nat. Phot. **13**, 765 (2019)

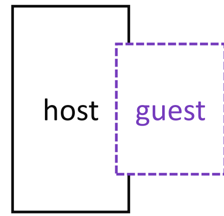
Energy band diagram of a single-layer OLED, with CzDBA is sandwiched between a MoO_3 (anode) and Al (cathode), using a thin C_{60} and TPBi interlayer for the formation of an Ohmic *h*- and *e*- contacts

JV and luminance-voltage characteristics of a CzDBA single-layer OLED (CzDBA is 75 nm) with (inset) EL spectrum, peaked at 560 nm. (b) EQE and power efficiency as a function of luminance.

OLED Emissive Layer: Host-Guest System

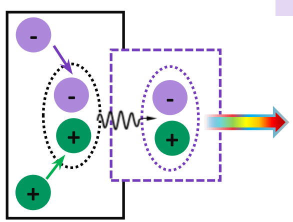
host-guest system: dye is dispersed in a matrix to prevent luminescence quenching

matrix
- capable of *transporting electrons* and *holes*
- *good thin film* forming properties
- *high luminescence efficiency*
- *wide optical bandgap* (compared to dopant)
- *should not quench* luminescence

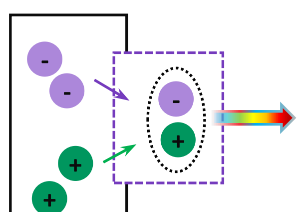


dopant
- ***high luminescence efficiency***
- ***absorption*** with strong overlap with emission of host
- ***narrow emission*** (for pure chromaticity)

light emission mechanisms depends on the ***site of exciton formation***



energy transfer: *electrons and holes forms exciton at host molecule site*, forming an excited state. The excited state energy is then transferred to the dopant molecule and excitons are then formed at the dopant molecular site. Emission is due to excited states of dopant molecule (thus independent of host)



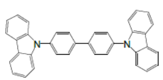
charge transfer: electrons and holes are directly injected into the dopant molecule and recombination occurs at the dopant molecular site

OLED Materials: Host Materials

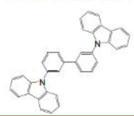
Phosphorescent

CBP family (carbazole)

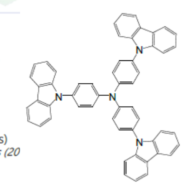
LT-E409 | CBP
4,4'-Bis(carbazol-9-yl)biphenyl
CAS No. : 58328-31-7
Grade : Sublimed, > 99.5% (HPLC)
Formula : $C_{36}H_{24}N_2$
M.W. : 484.59 g/mole
UV : 292, 318 nm (in THF)
PL : 369 nm (in THF)
TGA : > 320 °C (0.5% weight loss)



LT-N4069 | m-CBP
3,3'-Di(9H-carbazol-9-yl)biphenyl
CAS No. : 342638-54-4
Grade : Sublimed, > 99% (HPLC)
Formula : $C_{36}H_{24}N_2$
M.W. : 484.59 g/mole
UV : 292, 328 nm (in CH_2Cl_2)
PL : 349 nm (in THF)
TGA : > 250 °C (0.5% weight loss)
Reference : 1. Organic Electronics 12 (2011) 1711-1715 2. Adv. Mater. 2011, 23, 1436-1441

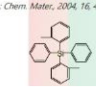


LT-E207 | TcTa
4,4',4''-Tris(carbazol-9-yl)triphenylamine
CAS No. : 139092-78-7
Grade : Sublimed, > 99.5% (HPLC)
Formula : $C_{54}H_{36}N_4$
M.W. : 740.89 g/mole
UV : 293, 326 nm (in THF)
PL : 385 nm (in THF)
TGA : > 410 °C (0.5% weight loss)
Reference : Physical Chemistry Chemical Physics (2015(38), 15850-15855.

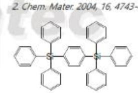


UGH family (phenyl)

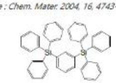
LT-N4008 | UGH-1
Bis(2-methylphenyl)diphenylsilane
CAS No. : 18849-24-6
Grade : Sublimed, > 99% (HPLC)
Formula : $C_{26}H_{24}Si$
M.W. : 364.55 g/mole
UV : 265 nm (in CH_2Cl_2)
PL : 298 nm (in CH_2Cl_2)
Reference : Chem. Mater. 2004, 16, 4743-4747



LT-N448 | UGH-2
1,4-Bis(triphenylsilyl)benzene
CAS No. : 40491-34-7
Grade : Sublimed, > 99% (HPLC)
Formula : $C_{42}H_{34}Si_2$
M.W. : 594.89 g/mole
UV : 265 nm (in CH_2Cl_2)
PL : 296 nm (in CH_2Cl_2)
TGA : > 270 °C (0.5% weight loss)
Reference : 1. Applied Physics Letters, 86, 263502 (2005) 2. Chem. Mater. 2004, 16, 4743-4747

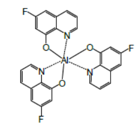


LT-N449 | UGH-3
1,3-Bis(triphenylsilyl)benzene
CAS No. : 18920-16-6
Grade : Sublimed, > 99% (HPLC)
Formula : $C_{42}H_{34}Si_2$
M.W. : 594.89 g/mole
UV : 265 nm (in THF)
PL : 301, 418 nm (in THF)
TGA : > 270 °C (0.5% weight loss)
Reference : Chem. Mater. 2004, 16, 4743-4747

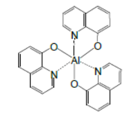


Fluorescent

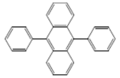
LT-N4091 | 6FAlq3
Tris(6-fluoro-8-hydroxy-quinolinato)aluminium
CAS No. : 1257308-66-9
Grade : > 99% (NMR)
Formula : $C_{27}H_{15}AlF_3N_3O_3$
M.W. : 513.4 g/mole
UV : 375 nm (in CH_2Cl_2)
PL : 495 nm (in CH_2Cl_2)
TGA : > 220 °C (0.5% weight loss)
Reference : Chemistry - A European Journal (2011), 17(33), 9076-9082



LT-E401 | Alq3
Tris(8-hydroxy-quinolinato)aluminium
CAS No. : 2085-33-8
Grade : Sublimed, > 99.5% (HPLC)
Formula : $C_{27}H_{18}AlN_3O_3$
M.W. : 459.43 g/mole
UV : 259 nm (in THF)
PL : 512 nm (in THF)
TGA : > 270 °C (0.5% weight loss)

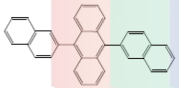


LT-N4084 | ADP
9,10-Diphenylanthracene
CAS No. : 1499-10-1
Grade : Sublimed, > 99%
Formula : $C_{26}H_{18}$
M.W. : 330.42 g/mole
TGA : > 150 °C (0.5% weight loss)
Reference : Journal of Chemical Education (2013), 90(6), 786-789

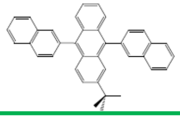


anthracene family

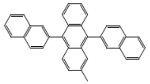
LT-E403 | ADN
9,10-Di(naphth-2-yl)anthracene
CAS No. : 122648-99-1
Grade : Sublimed, > 99.5% (HPLC)
Formula : $C_{34}H_{22}$
M.W. : 430.54 g/mole
UV : 375, 395 nm (in THF)
PL : 425 nm (in THF)
TGA : > 290 °C (0.5% weight loss)



LT-E404 | TBADN
2-*tert*-Butyl-9,10-di(naphth-2-yl)anthracene
CAS No. : 274905-73-6
Grade : Sublimed, > 99% (HPLC)
Formula : $C_{38}H_{30}$
M.W. : 486.64 g/mole
UV : 375, 395 nm (in THF)
PL : 431 nm (in THF)
TGA : > 290 °C (0.5% weight loss)



LT-E410 | MADN
2-Methyl-9,10-bis(naphthalen-2-yl)anthracene
CAS No. : 804560-00-7
Grade : Sublimed, > 99.5% (HPLC)
Formula : $C_{35}H_{24}$
M.W. : 444.57 g/mole
UV : 379, 399 nm (in CH_2Cl_2)
PL : 439 nm (in CH_2Cl_2)
TGA : > 300 °C (0.5% weight loss)

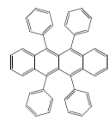


materials from http://www.lumtec.com.tw/

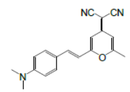
OLED Materials: Guest (dopant)

R

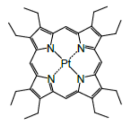
LT-E707 | Rubrene
5,6,11,12-Tetraphenylnaphthacene
UV : 299 nm (in THF)
PL : 553 nm (in THF)



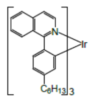
LT-E701 | DCM
(*E*)-2-(2-(4-(Dimethylamino)styryl)-6-methyl-4*H*-pyran-4-ylidene)malononitrile
UV : 462 nm (in THF)
PL : 577 nm (in THF)



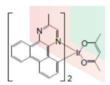
LT-N752 | PtOEP
Platium(II) octaethylporphine
UV : 389, 534 nm (in CH_2Cl_2)
PL : 649 nm (in CH_2Cl_2)



LT-N754 | Hex-Ir(piq)$_3$
Tris[2-(4-*n*-hexylphenyl)quinoline)]iridium(III)
UV : 325 nm (in CH_2Cl_2)
PL : 617 nm (in CH_2Cl_2)

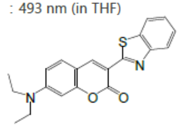


LT-N753 | Ir(MDQ)$_2$(acac)
Bis(2-methyldibenzo[*f,h*]quinoxaline)(acetylacetonate)iridium(III)
UV : 325, 428 nm (in CH_2Cl_2)
PL : 616 nm (in CH_2Cl_2)

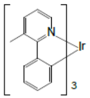


G

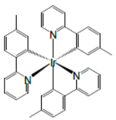
LT-E501 | Coumarin 6
3-(2-Benzothiazolyl)-7-(diethylamino)coumarin
UV : 443 nm (in THF)
PL : 493 nm (in THF)



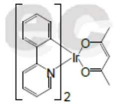
LT-N5002 | Ir(3mppy)$_3$
Tris(2-phenyl-3-methyl-pyridine)iridium
UV : 283, 383 nm (in CH_2Cl_2)
PL : 522 nm (in CH_2Cl_2)



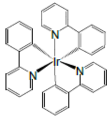
LT-N506 | Ir(mppy)$_3$
Tris[2-(*p*-tolyl)pyridine]iridium(III)
UV : 287, 373 nm (in CH_2Cl_2)
PL : 514 nm (in CH_2Cl_2)



LT-E505 | Ir(ppy)$_2$(acac)
Bis(2-phenylpyridine)(acetylacetonate)iridium(III)
UV : 259 nm (in THF)
PL : 524 nm (in THF)



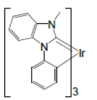
LT-E504 | *fac*-Ir(ppy)$_3$
fac-Tris(2-phenylpyridine)iridium(III)
UV : 282, 377 nm (in THF)
PL : 513 nm (in THF)



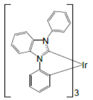
B

LT-E602 | Perylene
Perylene
UV : 410, 436 nm (in THF)
PL : 471 nm (in THF)

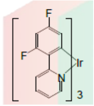
LT-N629 | *fac*-Ir(Pmb)$_3$
fac-Iridium(III) tris(1-phenyl-3-methylbenzimidazolin-2-ylidene-C,C$^{2'}$)
UV : 299 nm (in THF)
PL : 405 nm (in THF)



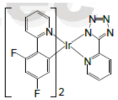
LT-N658 | *fac*-Ir(dpbic)$_3$
fac-Tris(1,3-diphenyl-benzimidazolin-2-ylidene-C,C$^{2'}$) iridium(III)
UV : 281, 302 nm (in CH_2Cl_2)
PL : 472 nm (in CH_2Cl_2)



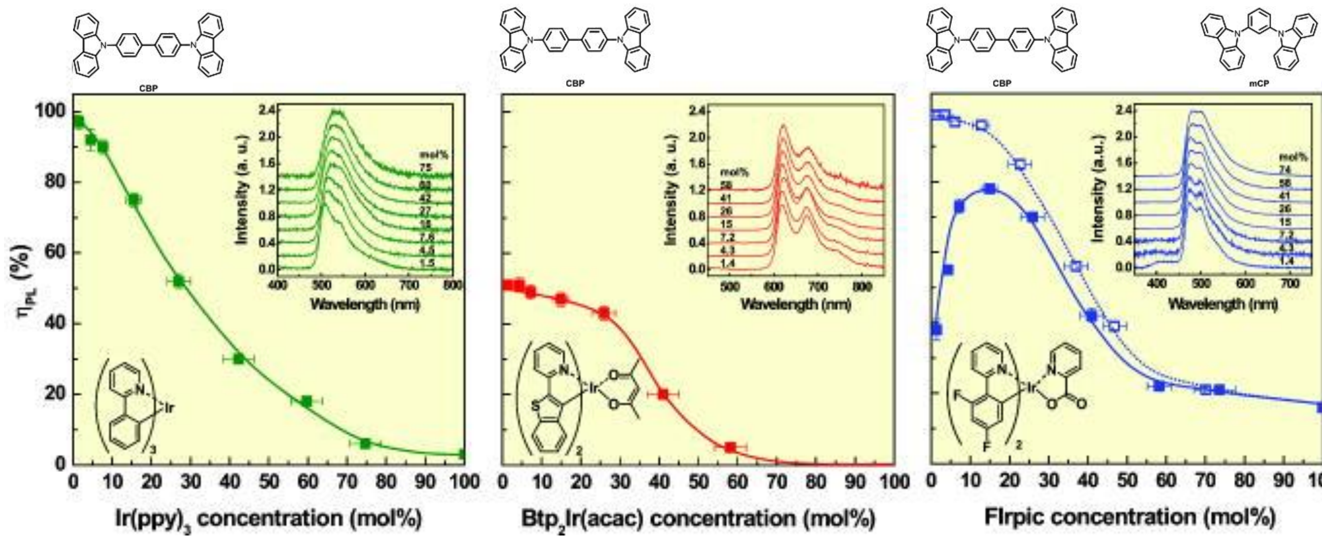
LT-N697 | Ir(Fppy)$_3$
Tris(2-(4,6-difuorophenyl)pyridine)iridium(III)
UV : 262 nm (in CH_2Cl_2)
PL : 493 nm (in CH_2Cl_2)



LT-N635 | FIrN4
Bis(2,4-difluorophenylpyridinato)(5-(pyridin-2-yl)-1*H*-tetrazolate) iridium(III)
UV : 368 nm (in THF)
PL : 459 nm (in THF)



RGB Emission in OLED



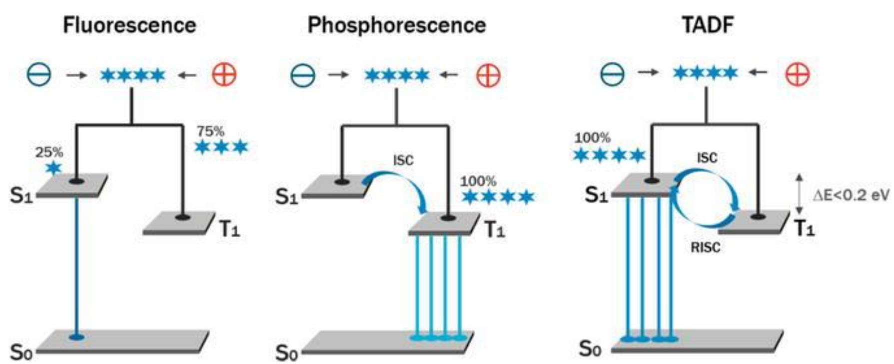
Appl. Phys. Lett. **86,** 071104 (2005)

PL quantum efficiency η_{PL} *vs.* dopant concentration in (a) **Ir(ppy)$_3$:CBP**; (b) **Btp$_2$Ir(acac):CBP**; and (c) **FIrpic:CBP** (■) and **FIrpic:mCP** (□). Insets show PL spectra of Ir(III) complex:CBP measured at each dopant concentration (increasing going up on y-axis): (a) 1.5-75mol%, (b) 1.4-58mol%; and (c) 1.4-74mol%.

Thermally-Activated Delayed Fluorescence (TADF)

Thermally **A**ctivated **D**elayed is a fluorescence-based mechanism which relies on fluorescencehe ***repopulation of the singlet state by reverse intersystem crossing (RISC) from the triplet state***, triggered by ***thermal energy***

→ (theoretical) internal quantum efficiency (IQE) is 100%



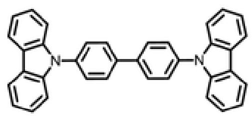
spatially separating molecule HOMO and ***LUMO*** using *e*-donating (donor) and *e*-withdrawing (acceptor) building blocks generates a charge-transfer structure with localized HOMO and LUMO orbitals.

- increasing the *twist angle* between the donor and acceptor moiety

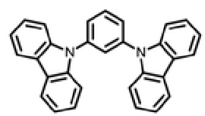
https://www.intechopen.com/books/luminescence-oled-technology-and-applications/tadf-technology-for-efficient-blue-oleds-status-and-challenges-from-an-industrial-point-of-view

Efficient TADF Emission: Requirements for HOST

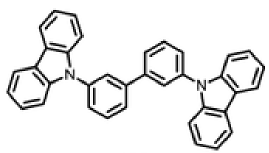
Phosphorescence and TADF both involve the triplet excitons in their emission channel,
→ Ph-OLEDs and TADF-OLEDs require emitter dispersion within hosts with higher triplet energy than the emitters



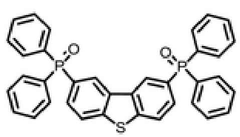
CBP



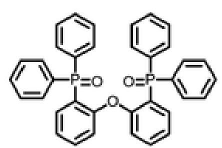
mCP



mCBP



PPT



DPEPO

Adv. Optical Mater. **7**, 1800565 (2019)

host properties

optical compatibility

hosts emission spectra overlap with dopant absorption spectra (to activate energy transfer mechanism)

thermal & morphological stability

high glass transition temperature (T_g) for stabilizing the film morphology and inhibiting crystallization

extended π-conjugation

fused ring systems lower the triplet energy (*i.e.* naphthalene less than biphenyl)

low polarity

reduce emitter-host local dipole interactions that tend to shift the emission peak to longer wavelengths

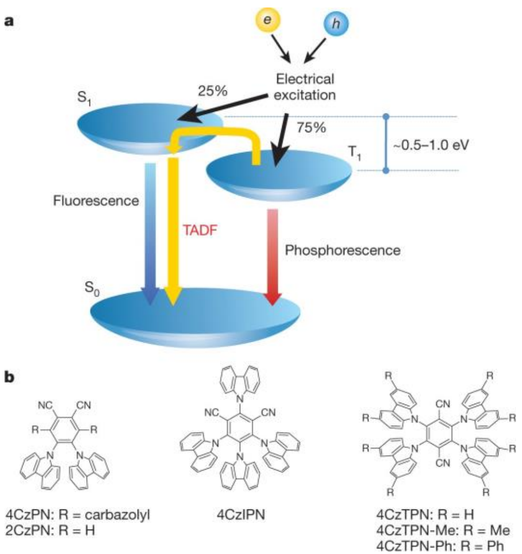
connection pattern & torsion angles

highly twisted molecular structures reduce the conjugation (increasing triplet level)

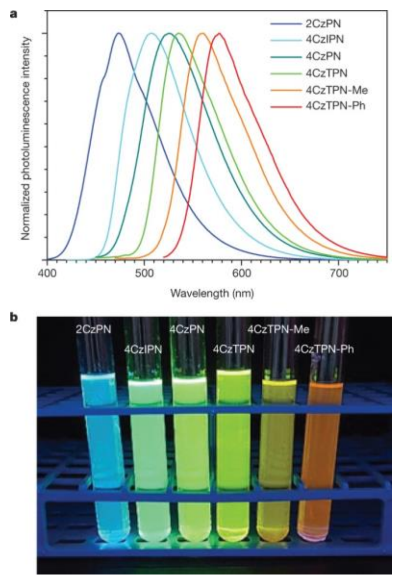
aggregation

bulky substituents weaken intermolecular reactions of π-conjugated host molecules, thus reducing the red-shift of phosphorescence spectra

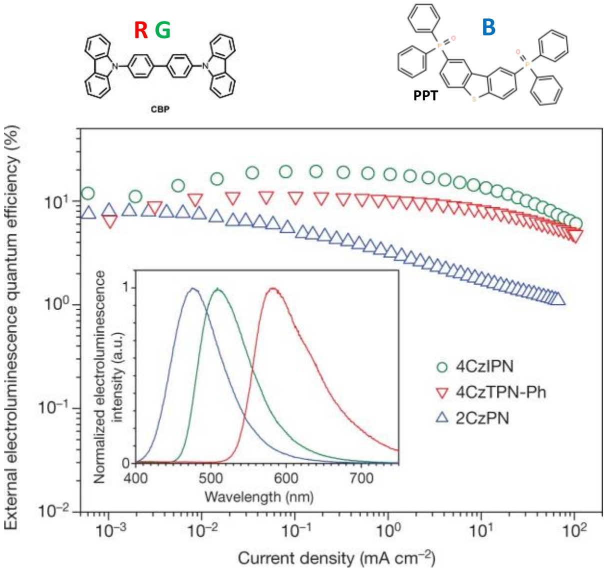
TADF-based OLED Devices



(a) Energy diagram of a conventional organic molecule and (b) molecular structures of TADF molecule (Me, methyl; Ph, phenyl).



(top) PL spectra measured in toluene and (bottom) photograph under UV irradiation (@365 nm).



Appl. Phys. Lett. **86,** 071104 (2005)

External EL quantum efficiency as a function of current density for OLEDs containing **4CzIPN**, **4CzTPN-Ph** and **2CzPN** as emitters. (Inset) EL of these OLEDs (colored accordingly) at a current density of 10 mA/cm^2

Summary

Today

Organic Light Emitting Diode (OLED)

- fundamental characteristics and mechanism
- materials (electrode, charge transport, emissive layer)
- TADF molecule to reach deep blue emitters

Next

Applications of Organic Light Emitting Diodes