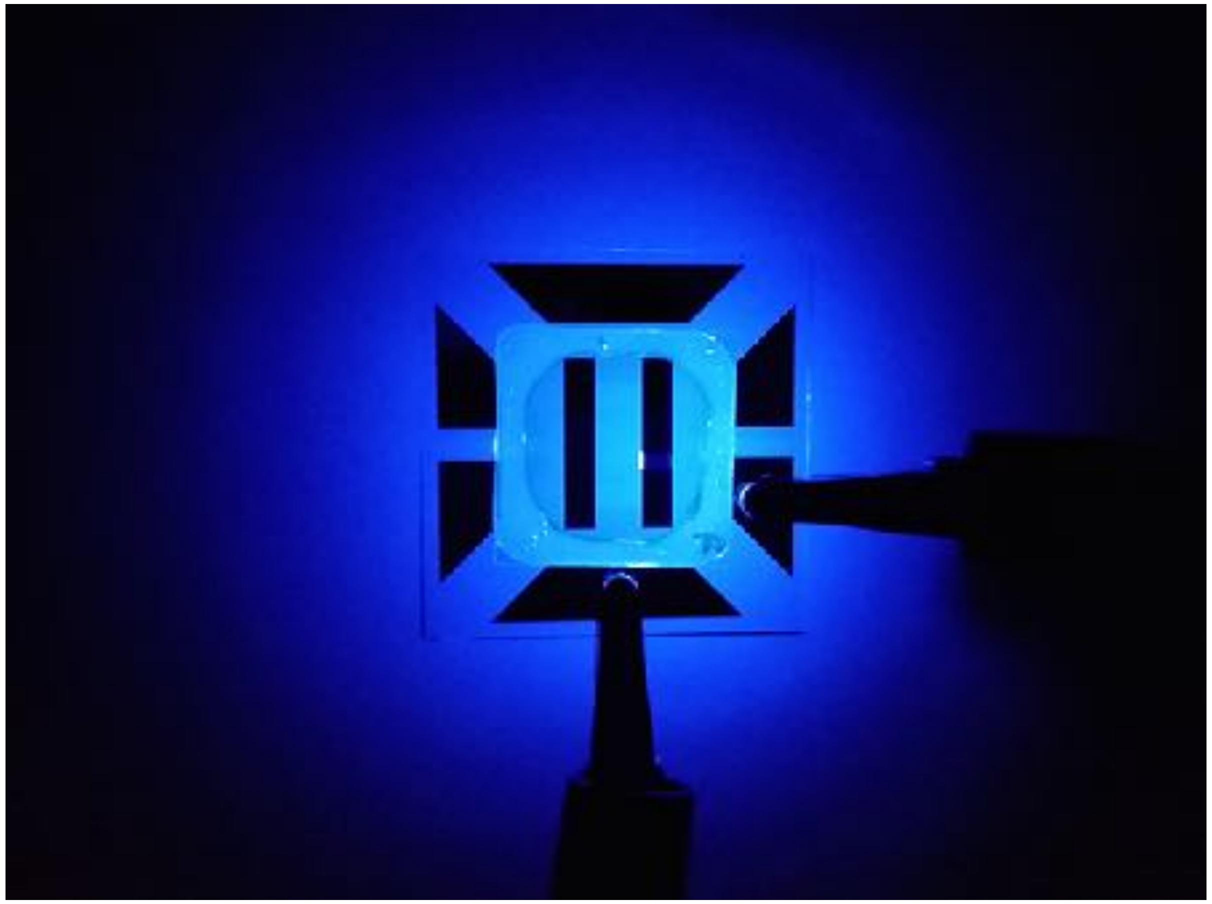
Phosphorescent OLEDs

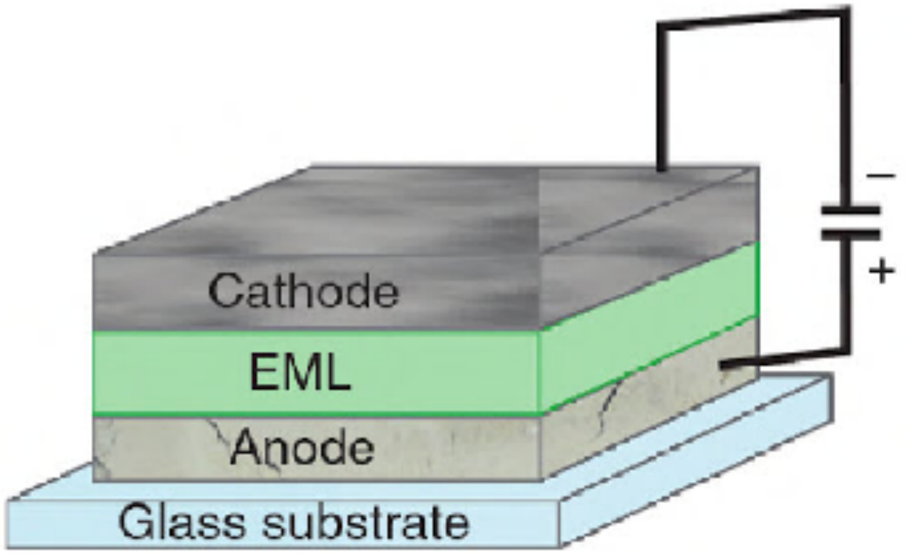


Jeffrey Lipshultz
MacMillan Lab Group Meeting
November 1, 2017

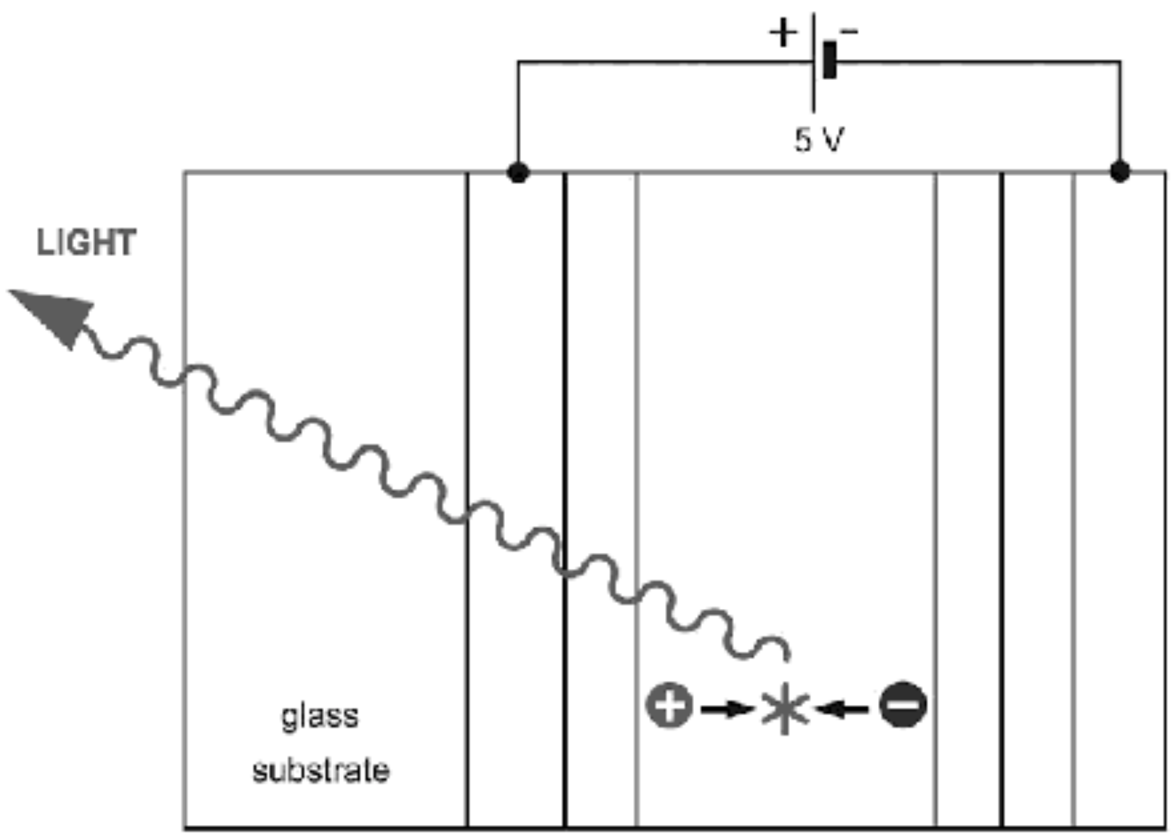
What is an Organic LED?

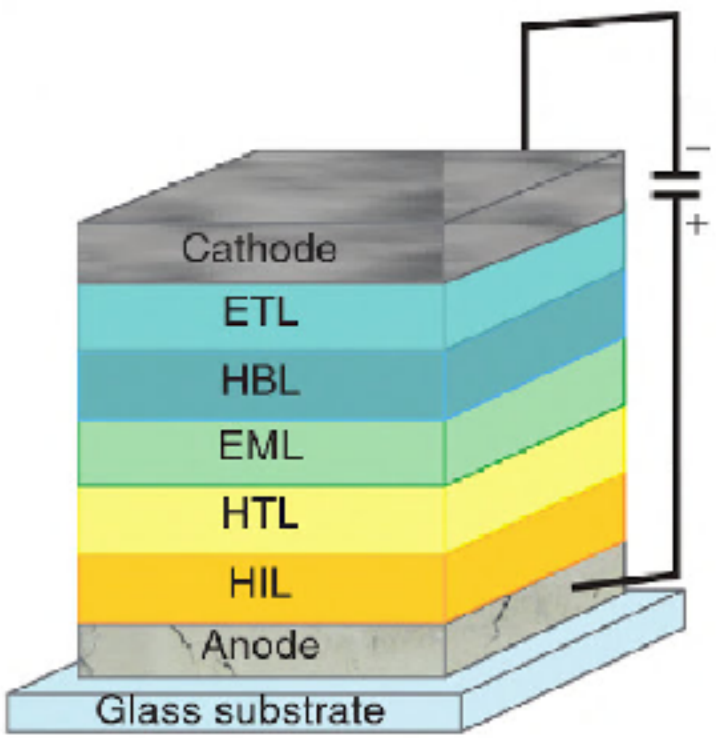
- Three basic components:

  1. Anode: inject holes (i.e. positive charges)
  2. Organic seminconductor Emission Layer (EML)
  3. Cathode: inject electrons



- How does it work?

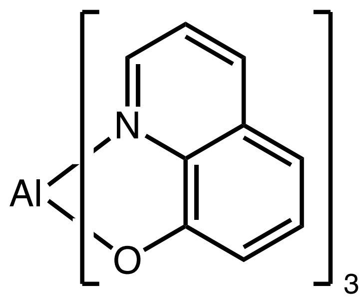




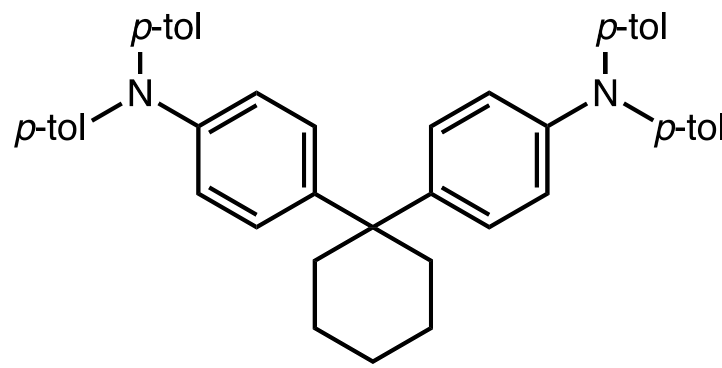
Hartmut, Y. *Highly Efficient OLEDs with Phosphorescent Materials*; Wiley-VCH: Weinheim, 2008.
Zysman-Colman, E. *Iridium(III) in Optoelectronic and Photonics Applications*; John Wiley & Sons Ltd: Hoboken, NJ, 2017.

Early OLEDs

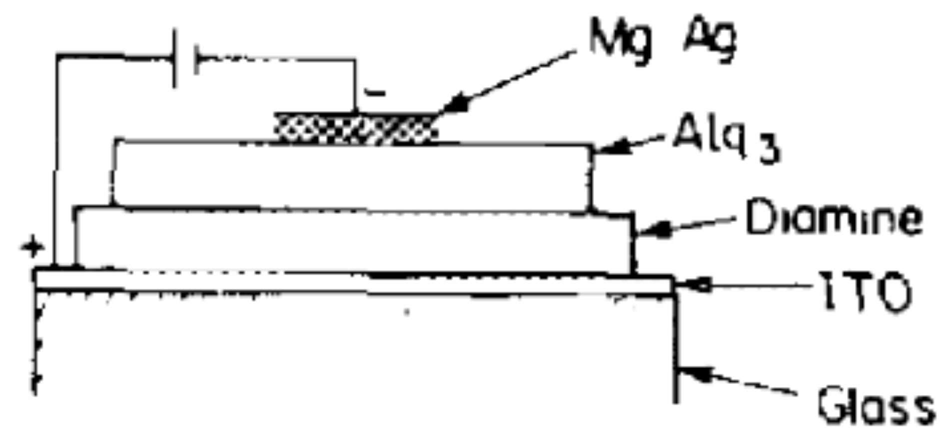
- 1987: First “practical” (> 1% EQE) OLED using Alq_3 (Eastman Kodak)



Alq_3



“diamine”



External Quantum Efficiency (EQE)

$$\eta_{ex} = \frac{\text{photons emitted}}{\text{electrons injected}}$$

Internal Quantum Efficiency (IQE)

$$\eta_i = \frac{\text{photons emitted}}{\text{excitons produced}}$$

Burroughes, J. H. *et. al. Nature* **1990**, *347*, 539.
Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.

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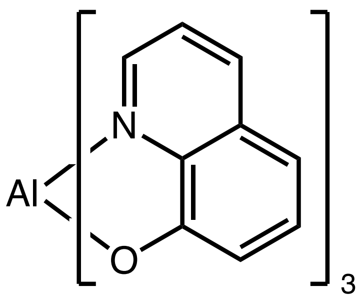
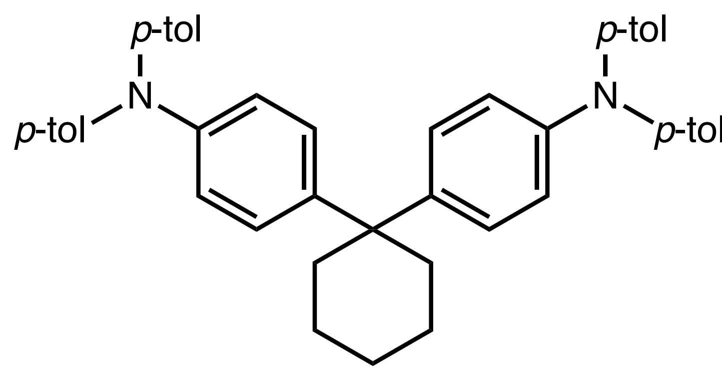
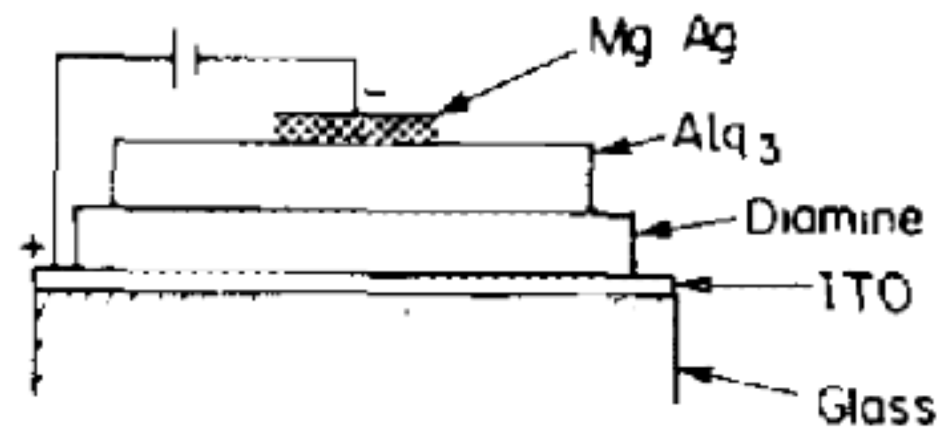


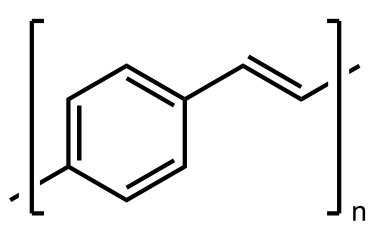
Alq_3



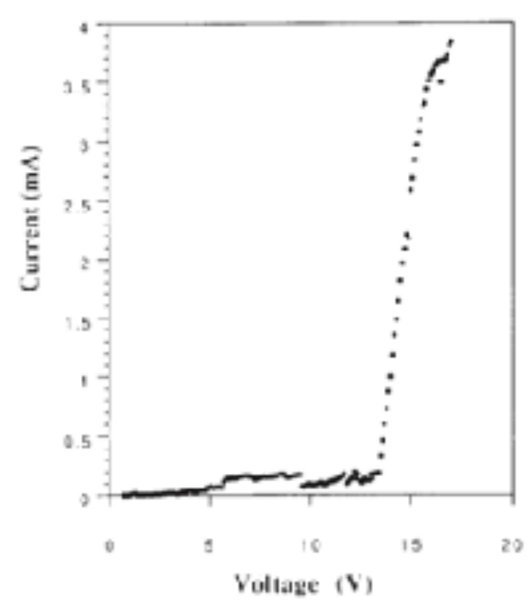
“diamine”

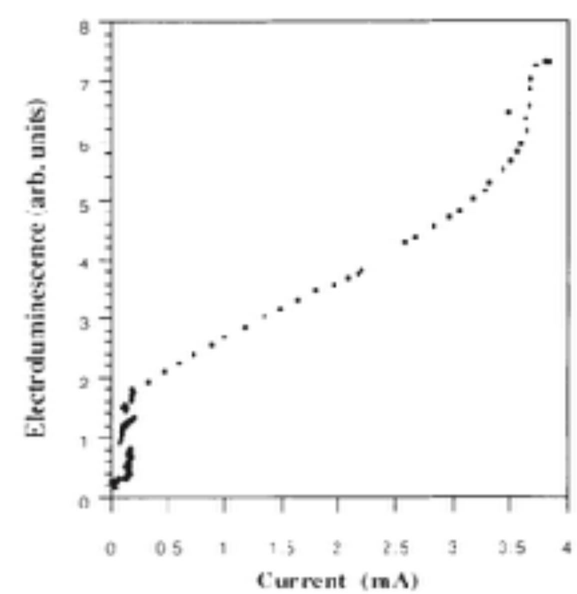


- 1990: First polymer-based OLED (~ 8% EQE) using PPV (Burroughes, Cambridge)



PPV



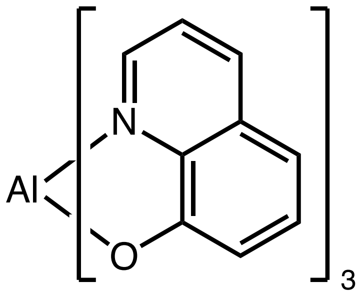


Burroughes, J. H. *et. al. Nature* **1990**, *347*, 539.
Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.

Fluorescent OLEDs: Limitations

- 1987: First "practical" (> 1% EQE) OLED using Alq_3 (Eastman Kodak)

Why only 1% EQE?



Alq_3

poor SOC means no emission from T_1

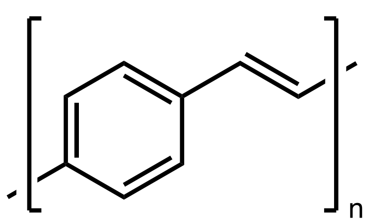
BUT

spin statistics dictate that excitons formed in 1:3 singlet:triplet ratio, somewhat verified experimentally

~25% IQE theoretical limit

$\chi_S = (20 \pm 1)\%$

- 1990: First polymer-based OLED (~ 8% EQE) using PPV (Burroughes, Cambridge)



PPV

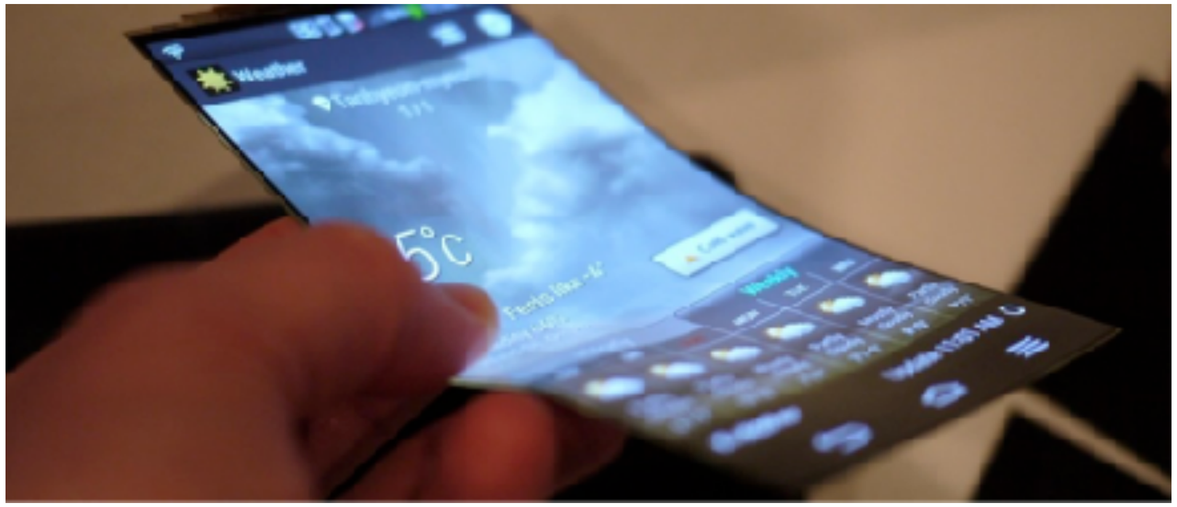
$\chi_S = (20 \pm 4)\%$
for MEH-PPV

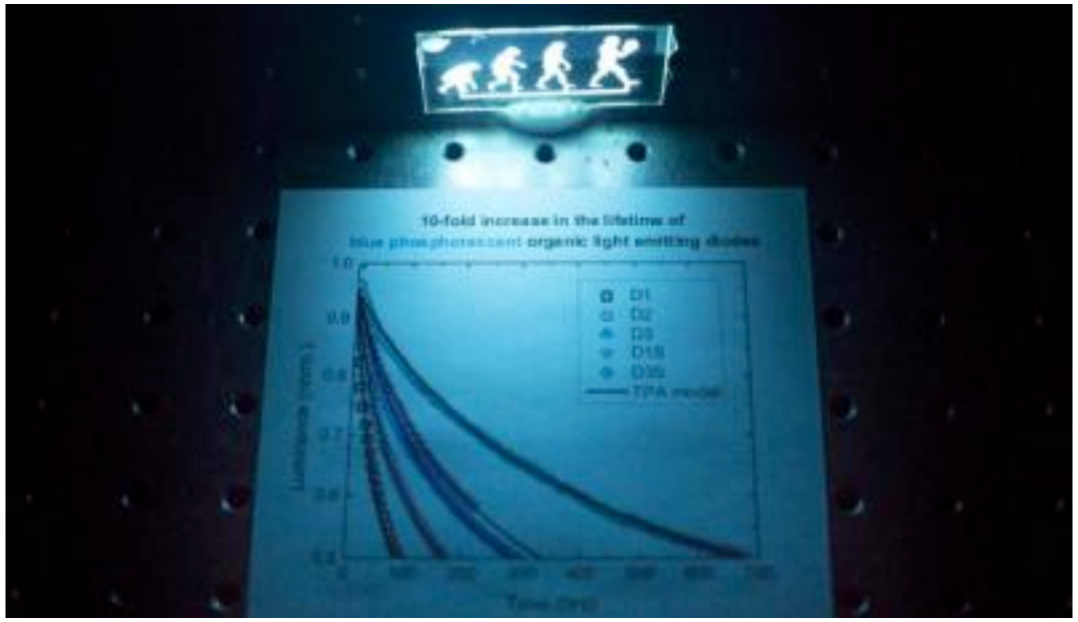
If <100% of excitons are available for luminescence, how do you improve efficiency?

Segal, M.; Baldo, M. A.; Holmes, R. J.; Forrest, S. R.; Soos, Z. G. *Phys. Rev. B.* **2003**, *68*, 075211.
Baldo, M. A.; O'Brien, D. F.; Thompson, M. E.; Forrest, S. R. *Phys. Rev. B.* **1999**, *60*, 14422.

Phosphorescent OLEDs

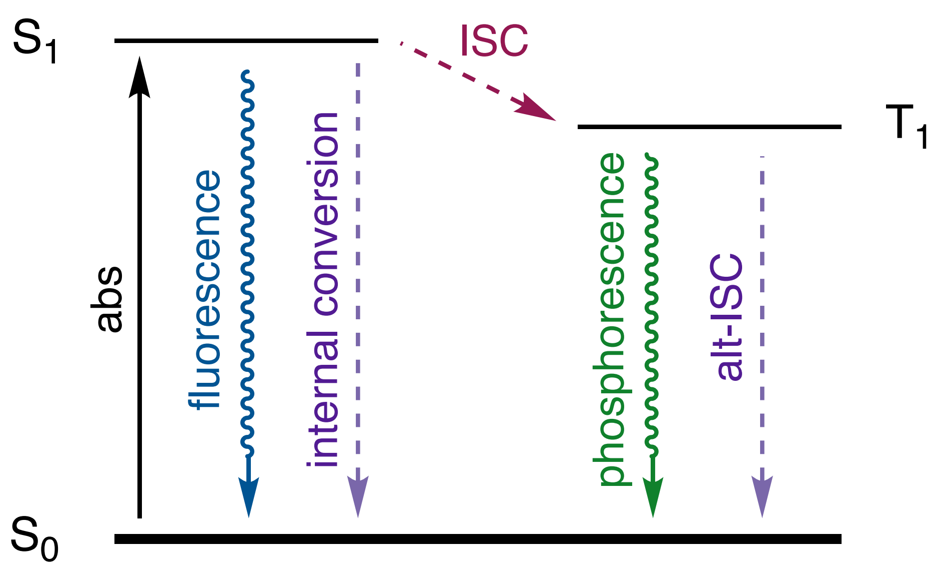
- The basics of PhOLEDs
  - Fluorescence vs. Phosphorescence
  - Basic design concept
  - Exciton formation/transfer
  - What makes a good dopant and host?
- PhOLED architectures and materials
  - Multi-layered devices
  - Phosphorescent emitters
  - Small-molecule and polymer hosts
  - Specific considerations
- Current state-of-the-art
  - Blue emitters!
  - WOLEDs via mixed fluorescence/phosphorescence
  - Thermally-activated delayed phosphorescence (TADF)



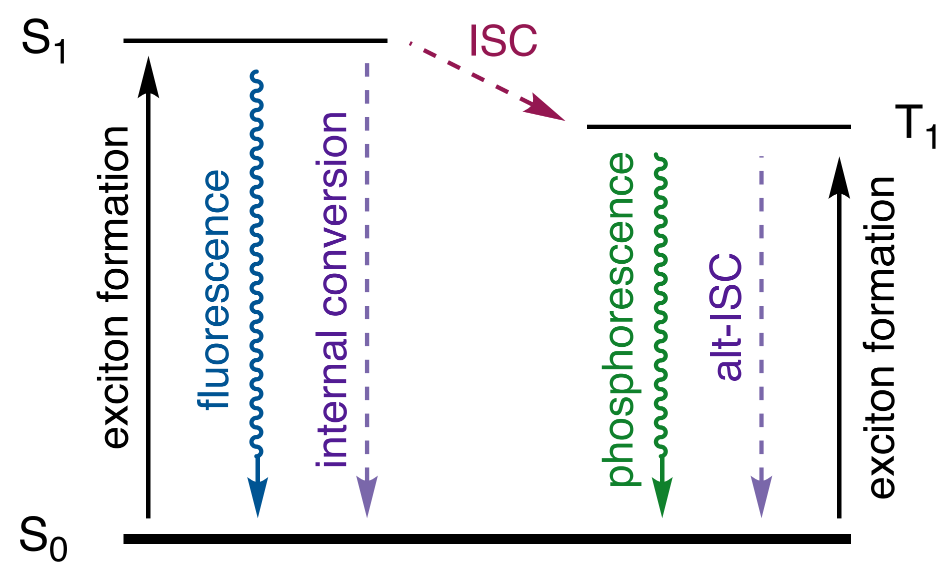


Fluorescence vs. Phosphorescence

Jablonski diagram upon photoexcitation



Jablonski diagram upon ***electro***excitation

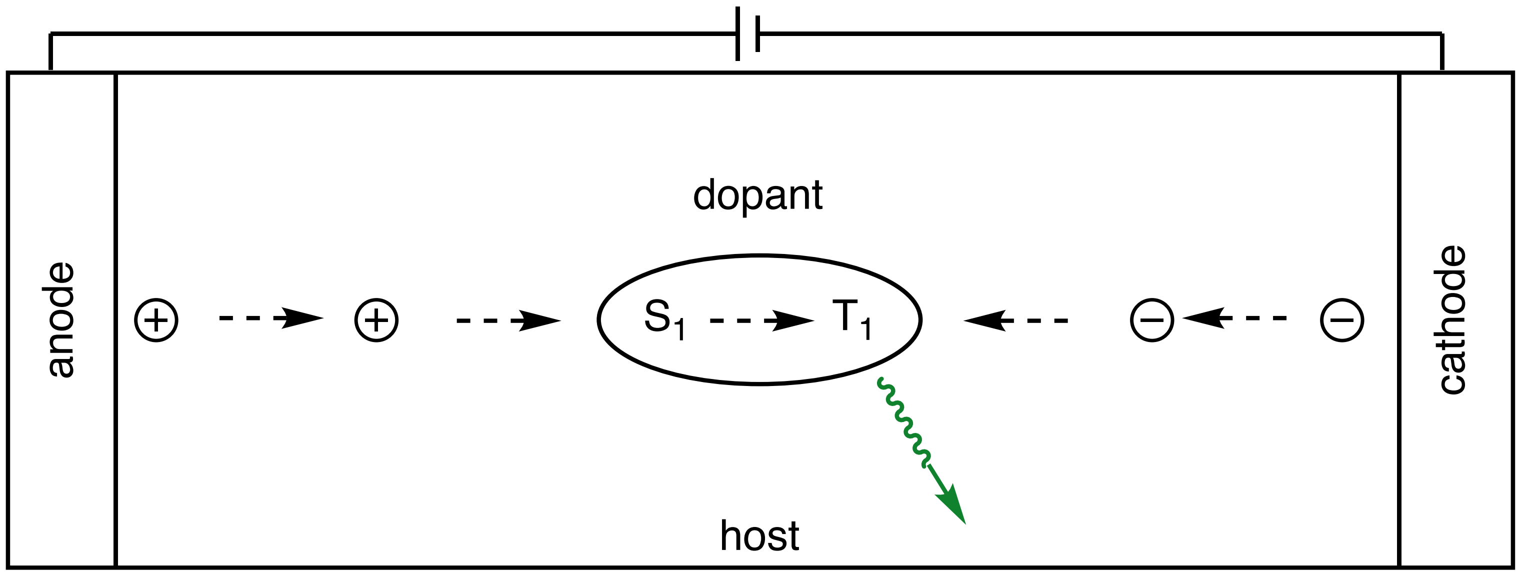


Key points for OLED development:

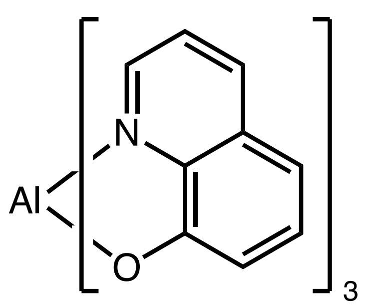
1. Efficient exciton-harvesting requires (?) triplet-harvesting
2. EL from T_1 requires appreciable SOC
3. T_1 lifetime much longer than S_1
4. $E(T_1) < E(S_1)$

Basic Design of PhOLEDs

- Host/guest or host/dopant EML



- 1998: First phosphor-doped OLED (Forrest, Princeton)



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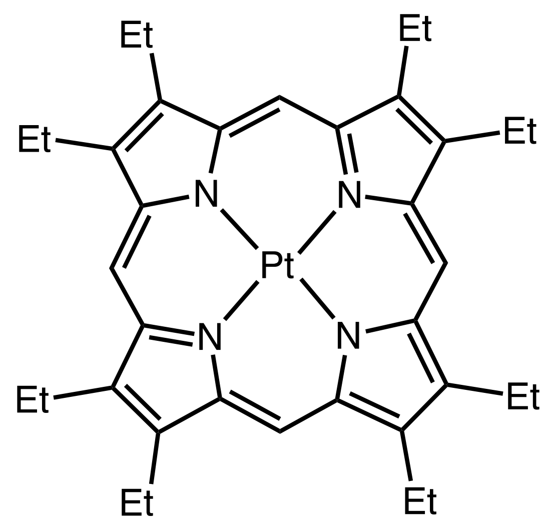


PtOEP

peak efficiencies:

$\eta_{ex} = 4\%$

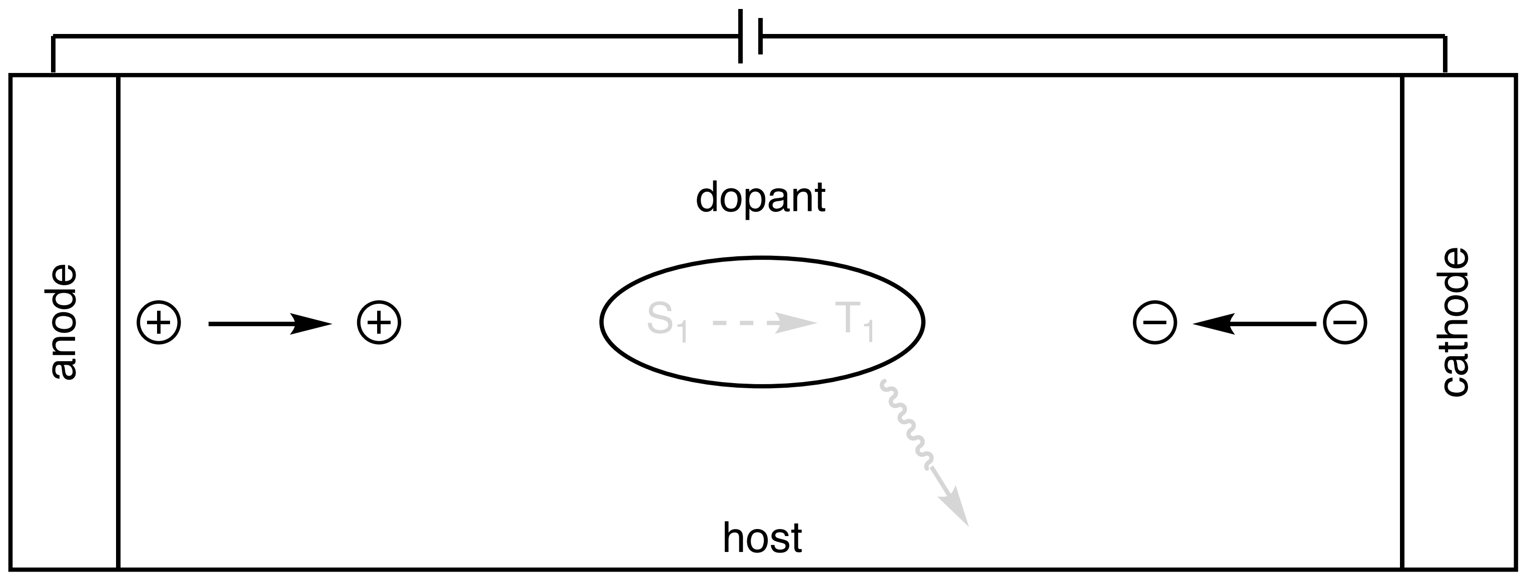
$\eta_i = 23\%$

EL lifetime 10-50 μs

Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoudtikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151.
Minaev, B.; Baryshnikov, G.; Agren, H. *Phys. Chem. Chem. Phys.* **2014**, *16*, 179.

Basic Principles of PhOLEDs

- Hole/electron recombination, aka exciton formation

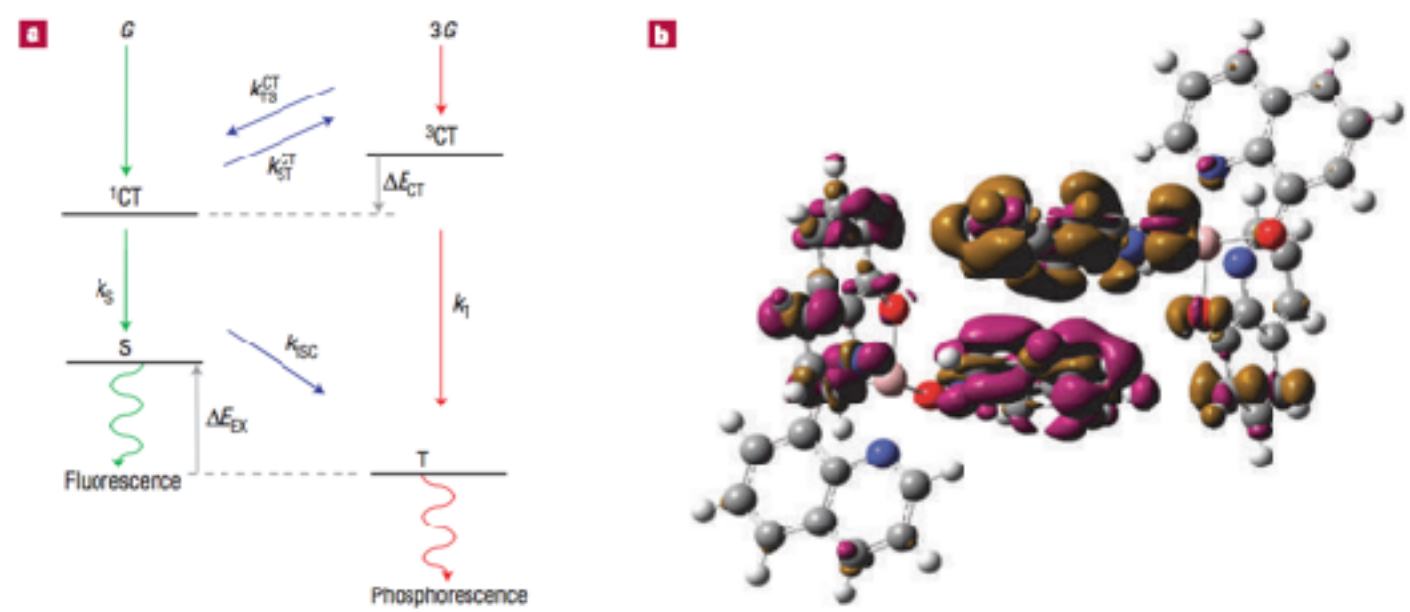


- As hole and electron get closer, Coloumbic attractions come into play

$$\Delta E(e\text{-}h) = \frac{e^2}{4\pi\varepsilon_0\varepsilon R_C} = k_B T$$

These associated h^+ and e^- are called a charge transfer (CT) state.

They don't necessarily need to be on a single molecule or polymer chain.



Segal, M.; Singh, M.; Rivoire, K.; Difley, S.; Van Coorhis, T.; Baldo, M. A. *Nature Mater.* **2007**, *6*, 374.
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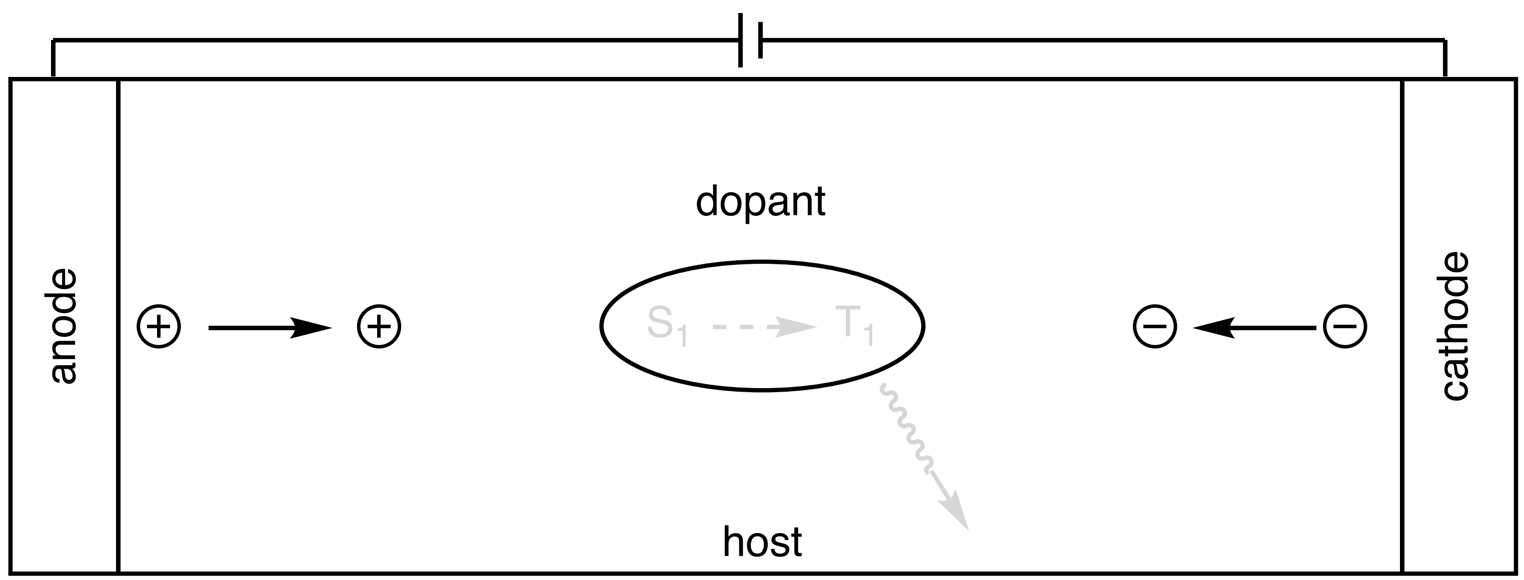
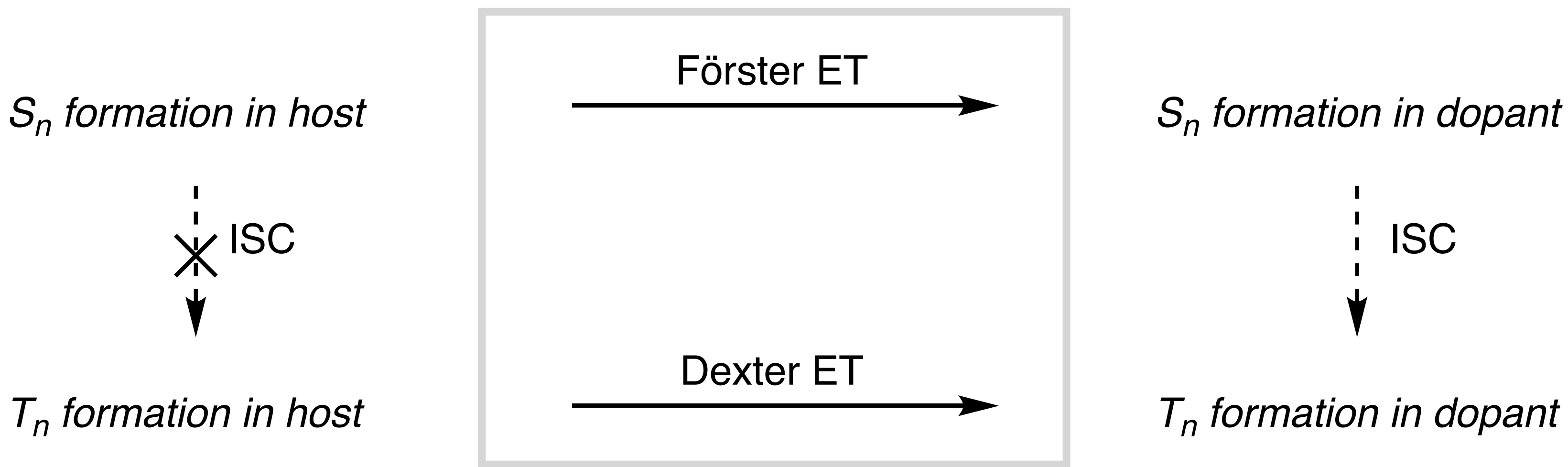


Four main scenarios for exciton formation:

exciton in host

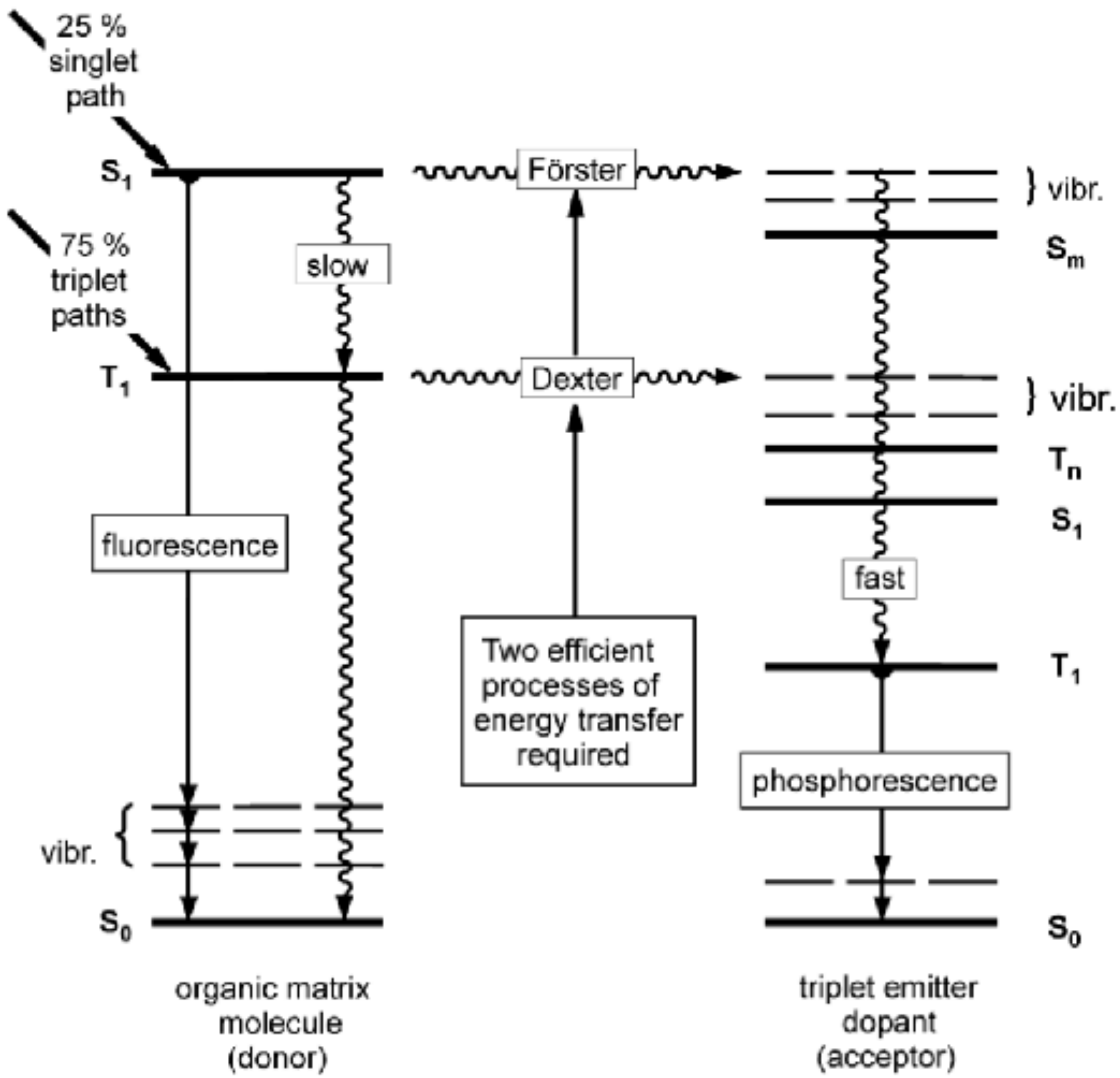
exciton in dopant



Reineke, S.; Baldo, M. A. *Phys. Status Solidi A* **2012**, *209*, 2341.
Hartmut, Y. *Highly Efficient OLEDs with Phosphorescent Materials*; Wiley-VCH: Weinheim, 2008.

Basic Principles of PhOLEDs

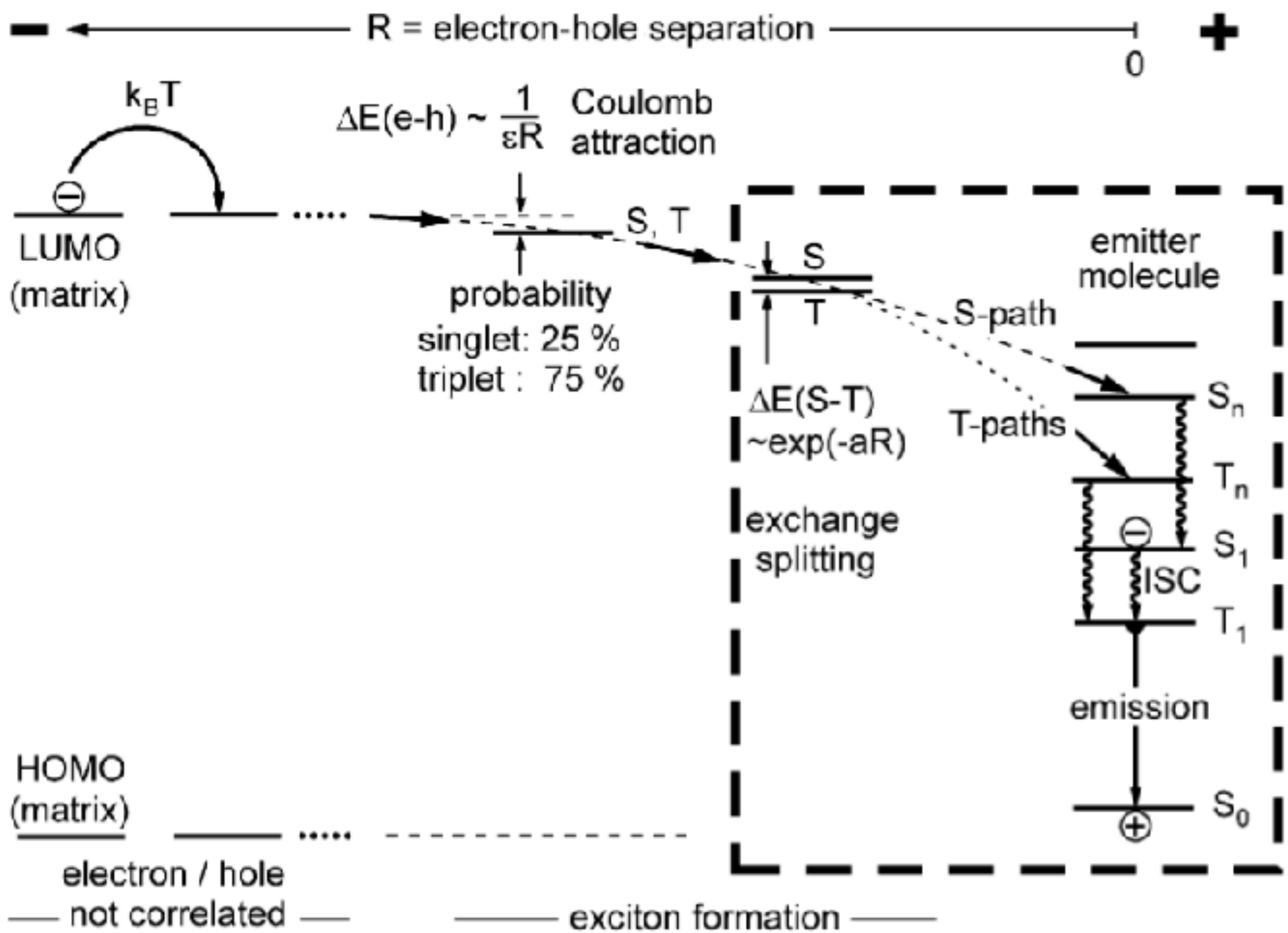
- Host exciton energy transfer to dopant exciton, ISC/relaxation, phosphorescence



Yersin, H. *Top. Curr. Chem.* **2004**, *241*, 1.
Hartmut, Y. *Highly Efficient OLEDs with Phosphorescent Materials*; Wiley-VCH: Weinheim, 2008.

Basic Principles of PhOLEDs

- Exciton formation on the dopant: hole trapping first



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Hartmut, Y. *Highly Efficient OLEDs with Phosphorescent Materials*; Wiley-VCH: Weinheim, 2008.

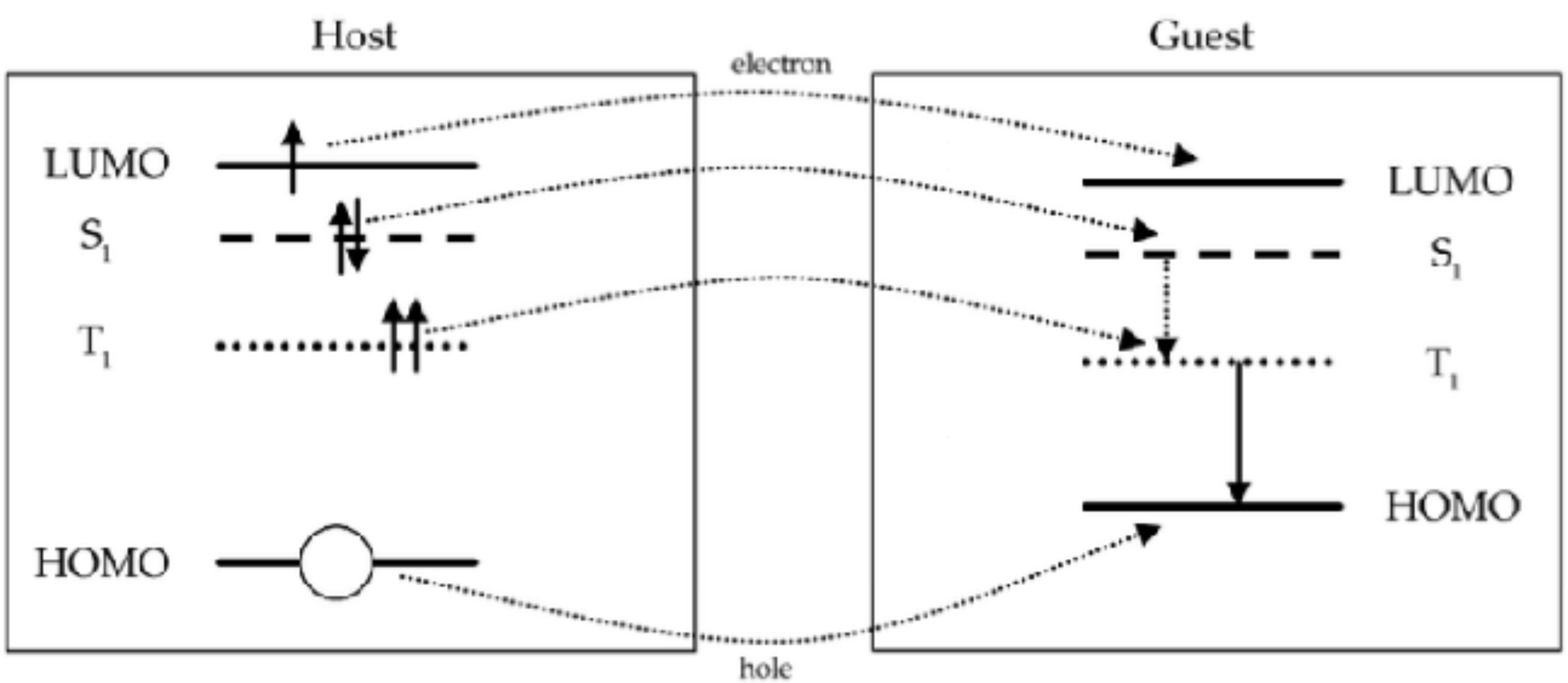
Basic Principles of PhOLEDs

characteristics of good PhOLED host

1. *Large HOMO-LUMO gap (high energy LUMO)*
2. *Long T_1 lifetime = non-phosphorescent = poor SOC*
3. *Higher energy S_1, T_1 than dopant*
4. *Can efficiently transfer h^+ or e^-, or both (ambipolar)*
5. *Spectral overlap (for FRET) and energy overlap (for DET)*

characteristics of good PhOLED dopant/emitter

1. *Lower LUMO than host*
2. *Shorter T_1 lifetime = phosphorescent = good SOC*
3. *Lower energy S_1, T_1 than host*
4. *Can efficiently trap h^+ or e^-, or both*
5. *Spectral overlap (for FRET) and energy overlap (for DET)*



Kappaun, S.; Slugove, C.; List, E. J. W. *Int. J. Mol. Sci.* ***2008***, 9, *1527.*
Tao, Y.; Yang, C.; Qin, J. *Chem. Soc. Rev.* **2011**, *40*, 2943.

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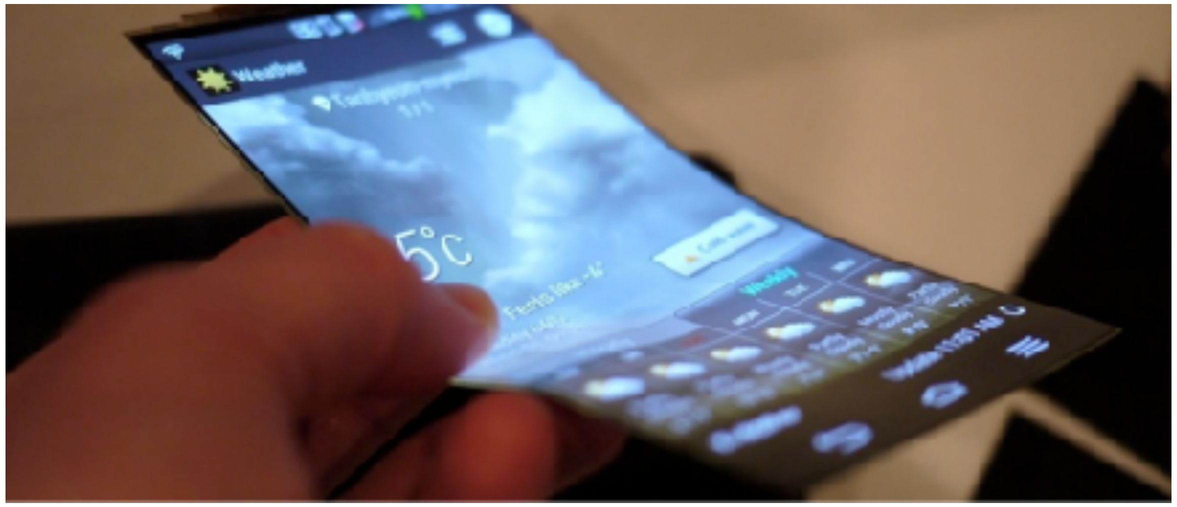
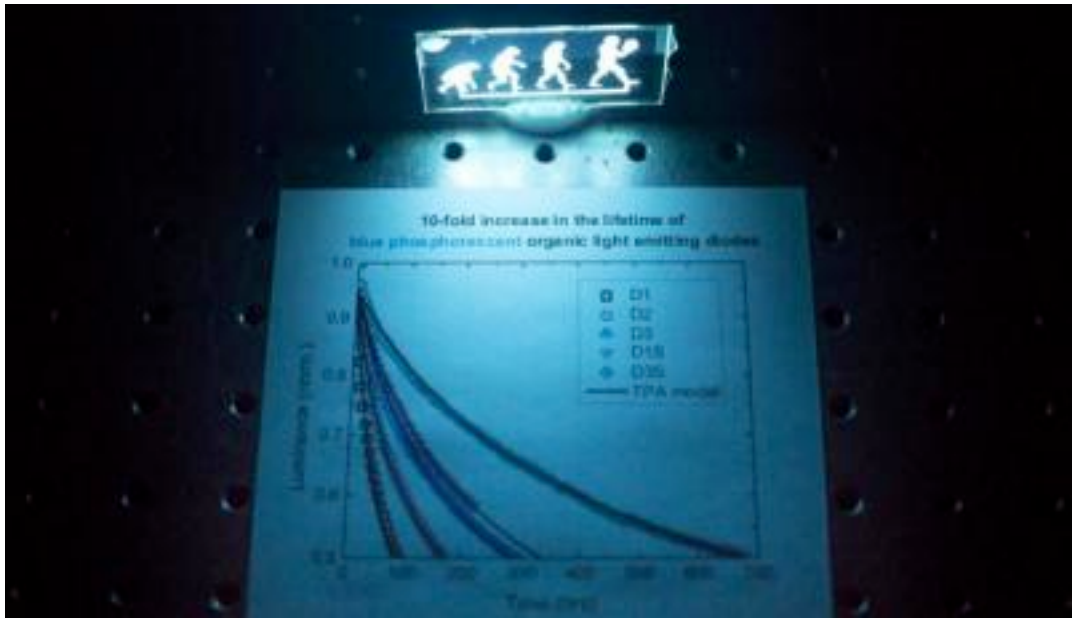
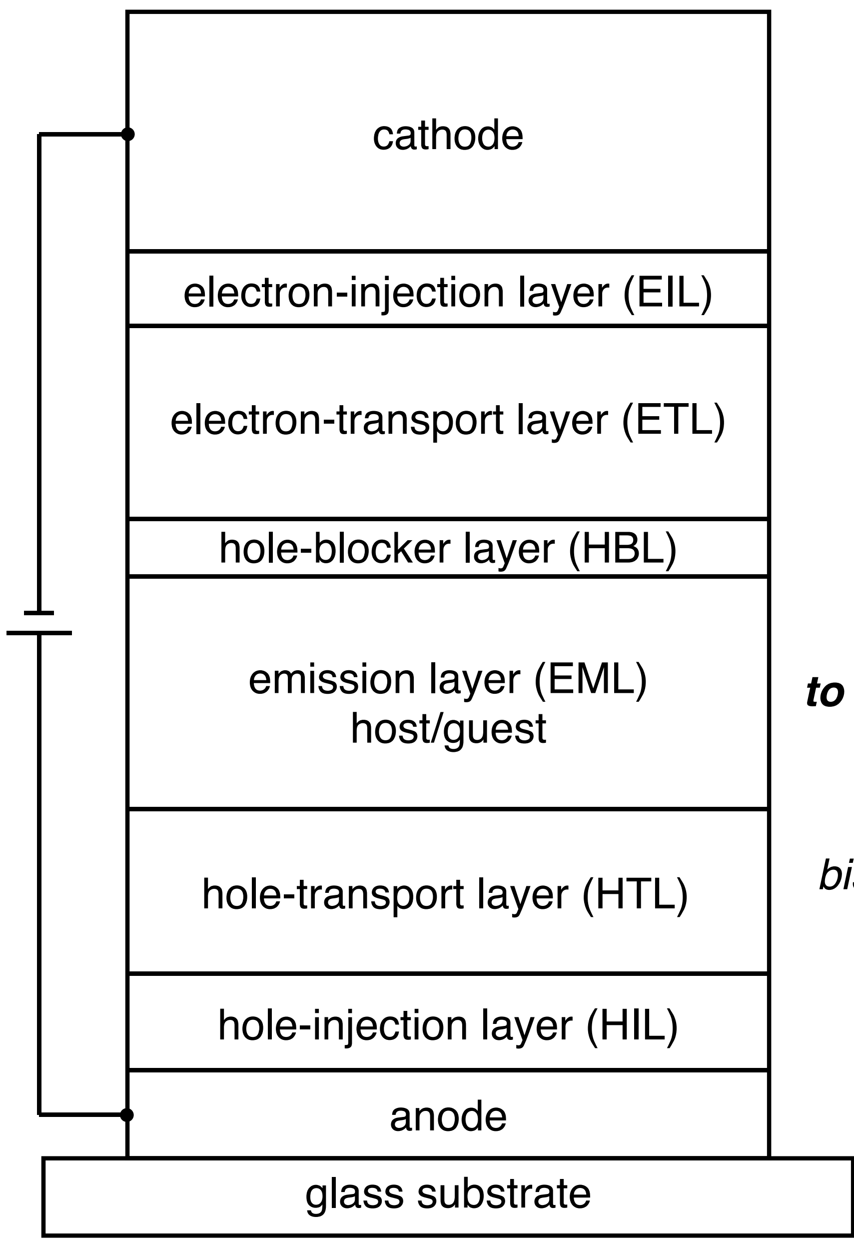




Mulitlayer OLED Device

representative multilayer PhOLED

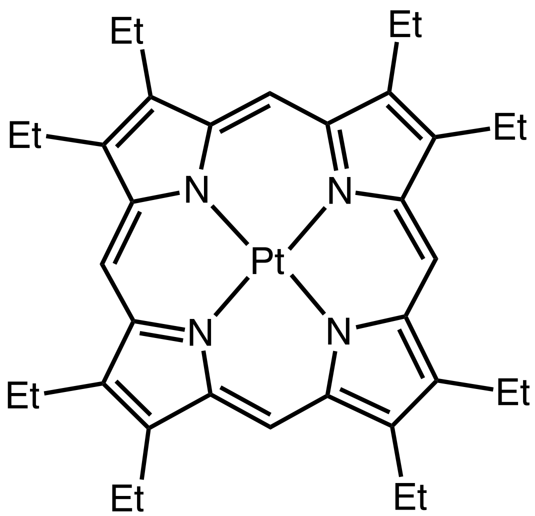


layer	examples	characteristics/roles
cathode	*Al, Mg/Ag, metals*	*… to be a cathode*
electron-injection layer (EIL)	*CsF, LiF*	*high LUMO*
electron-transport layer (ETL)	most common: *Alq$_3$*	*high E_T* *electron-deficient (pyridines)*
hole-blocker layer (HBL)	*bathocuproine (BCP)* ⇒	*prevent "unused" h^+* *from destroying ETL*
emission layer (EML) host/guest	***to be discussed in detail***	***transport h^+/e^- to form excitons***
hole-transport layer (HTL)	*bis(N,N'-diaryl)-biphenyls*	*high E_T* *electron-rich (triarylamines)*
hole-injection layer (HIL)	*PEDOT:PSS, [M]O$_n$*	*low HOMO*
anode	*ITO*	*ITO*

Kappaun, S.; Slugove, C.; List, E. J. W. *Int. J. Mol. Sci.* ***2008****,* 9*, 1527.*
Minaev, B.; Baryshnikov, G.; Agren, H. *Phys. Chem. Chem. Phys.* **2014**, *16*, 179.

Triplet-Emitting Dopants (Phosphors)

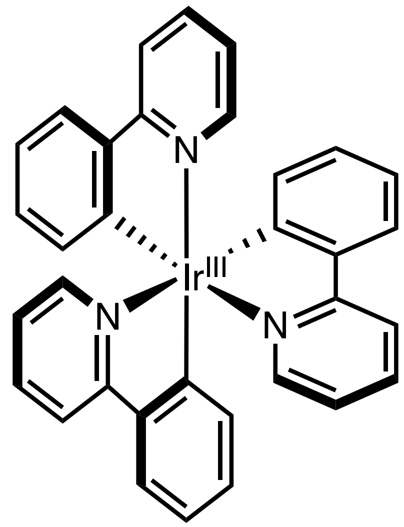
- Heavy-metal organometallic complexes exhibit appropriate phosphorescence



PtOEP

λ_{max} = 650 nm

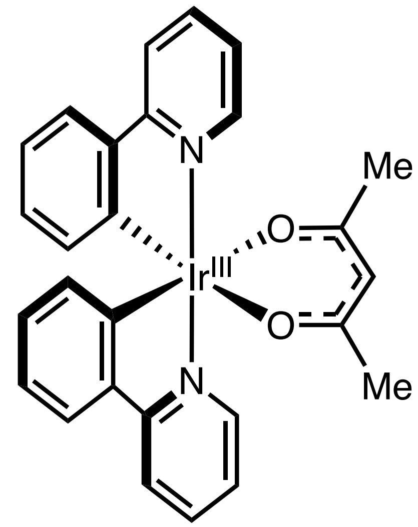
T_1 lifetime = 91 μs



Ir(ppy)$_3$

λ_{max} = 509 nm

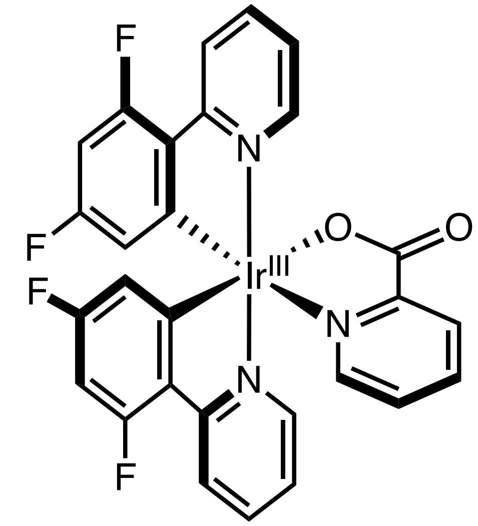
T_1 lifetime = 2.1 μs



Ir(ppy)$_2$(acac)

λ_{max} = 516 nm

T_1 lifetime = 1.6 μs



FIrpic

λ_{max} = 468 nm

T_1 lifetime = 1.7 μs

really long lifetime

high concentration of T_1

triplet-triplet annihilation

Chou, P.-T.; Chi, Y. *Chem. Eur. J.* **2007**, *13*, 380.
Nazeeruddin, M. K., *et al. Top. Curr. Chem.* **2017**, *375*, 39.
Hartmut, Y. *Highly Efficient OLEDs with Phosphorescent Materials*; Wiley-VCH: Weinheim, 2008.

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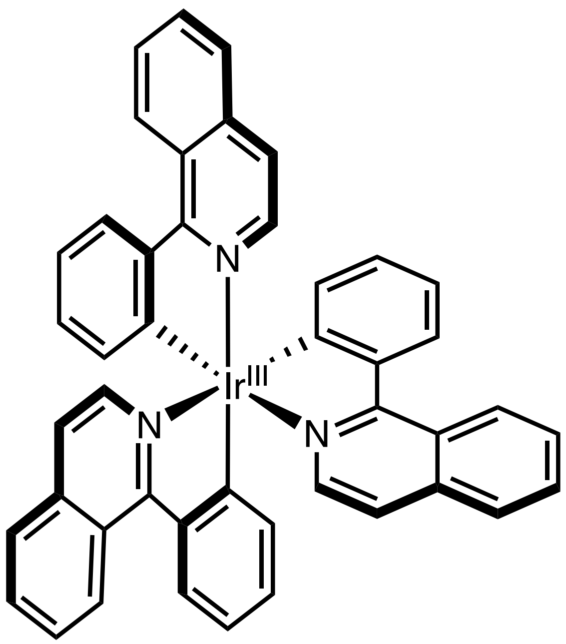
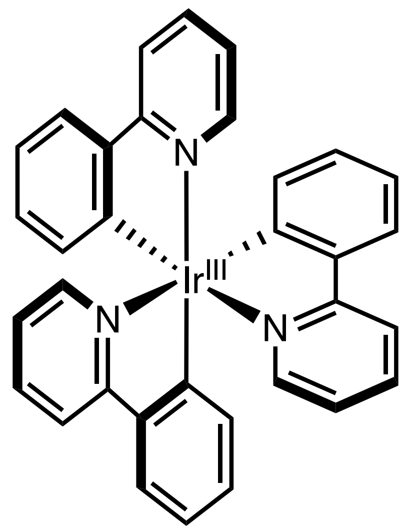


Ir(piq)$_3$

λ_{max} = 620 nm

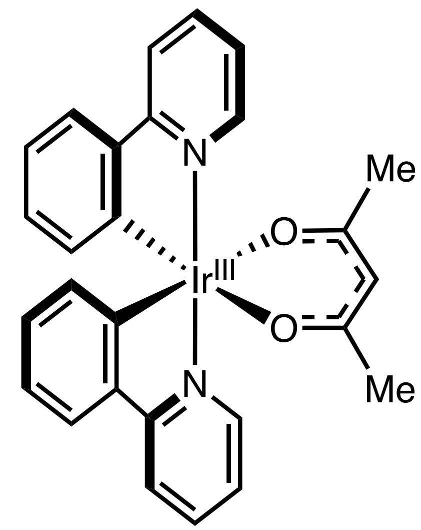
T_1 lifetime = 0.7 μs



Ir(ppy)$_3$

λ_{max} = 509 nm

T_1 lifetime = 2.1 μs



Ir(ppy)$_2$(acac)

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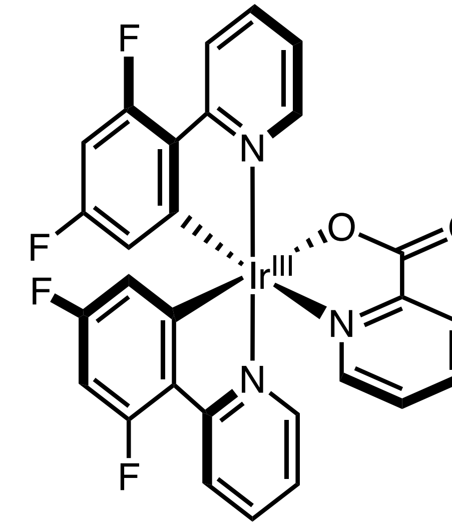
T_1 lifetime = 1.6 μs



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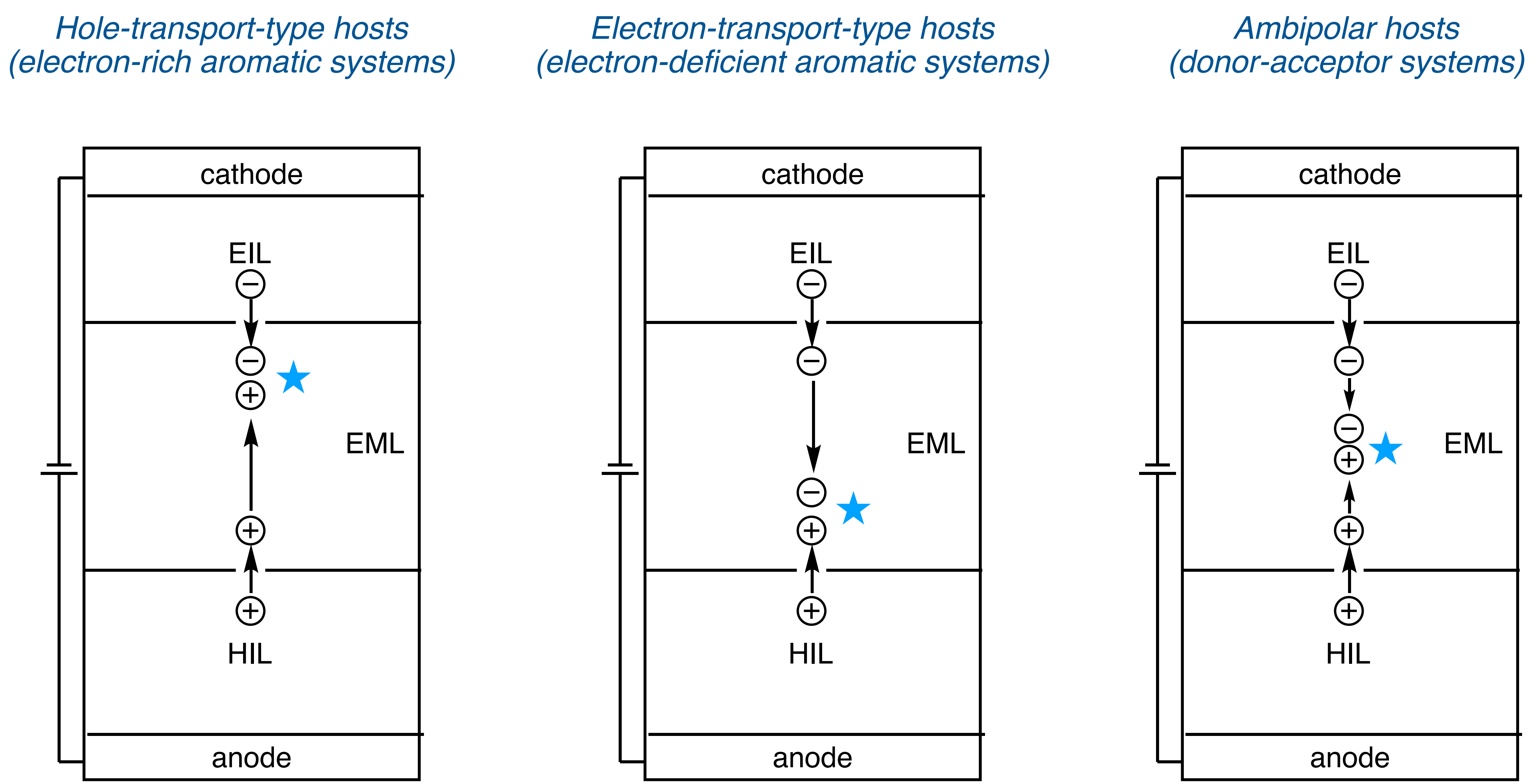
Host Materials for PhOLEDs



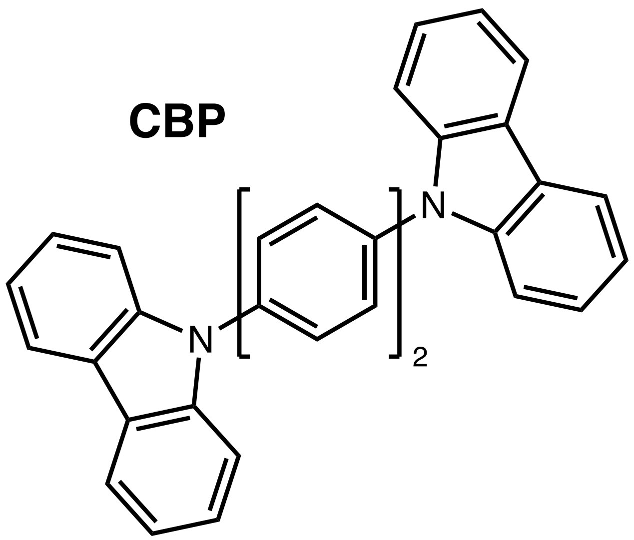
Type of host material determines exciton-generation zone

Tao, Y.; Yang, C.; Qin, J. *Chem. Soc. Rev.* **2011**, *40*, 2943.

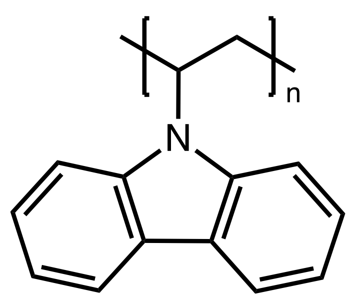
Host Materials for PhOLEDs

Hole-transport-type hosts
(electron-rich aromatic systems)

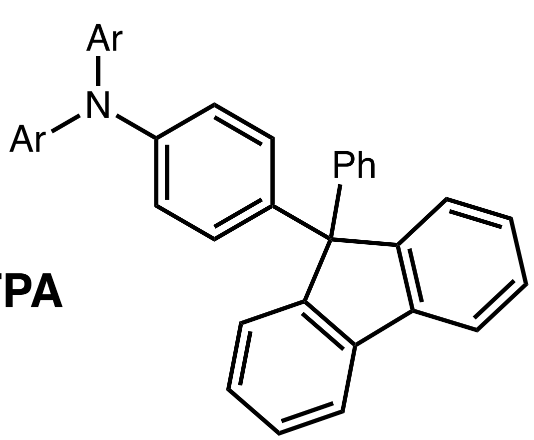
CBP



PVK

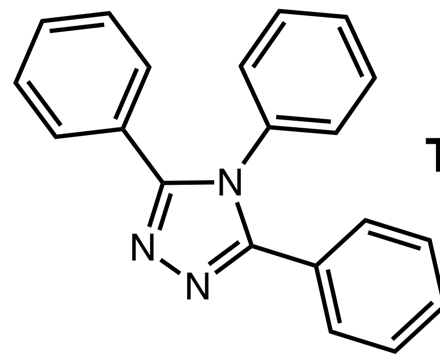


TFTPA

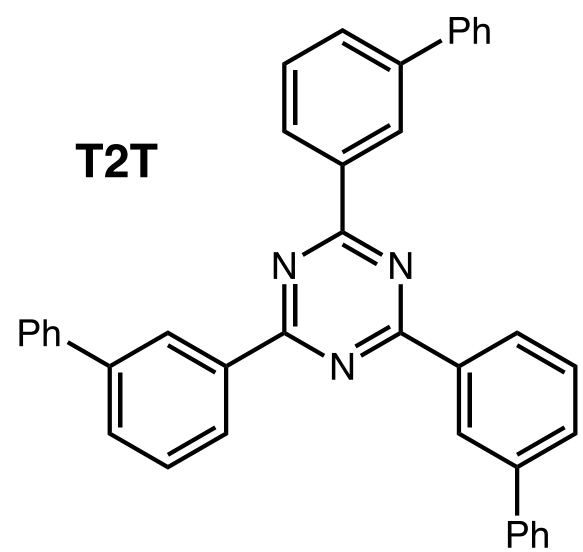


Electron-transport-type hosts
(electron-deficient aromatic systems)

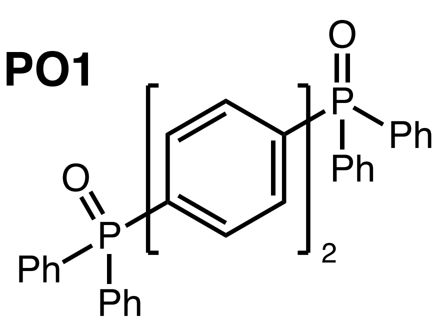
TAZ



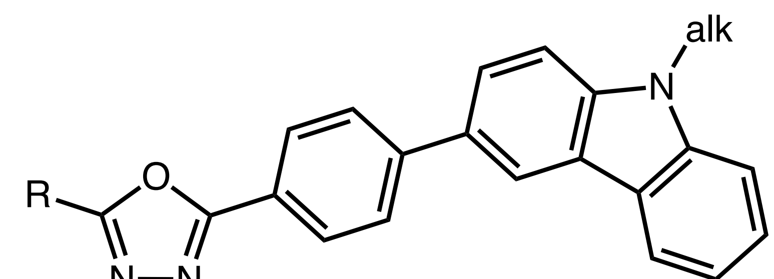
T2T



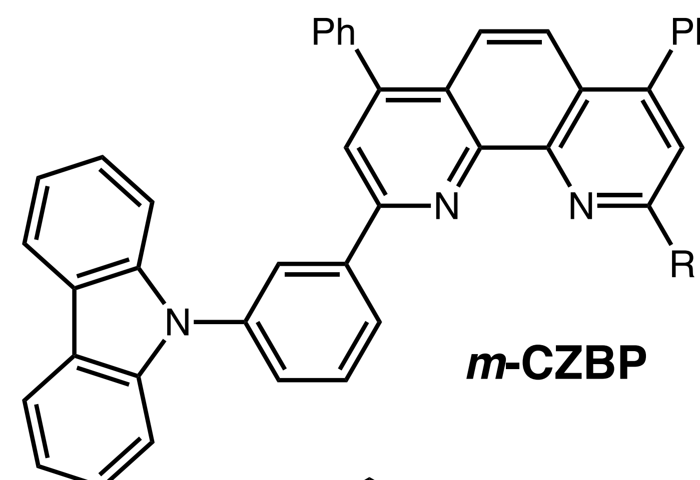
PO1



Ambipolar hosts
(donor-acceptor systems)

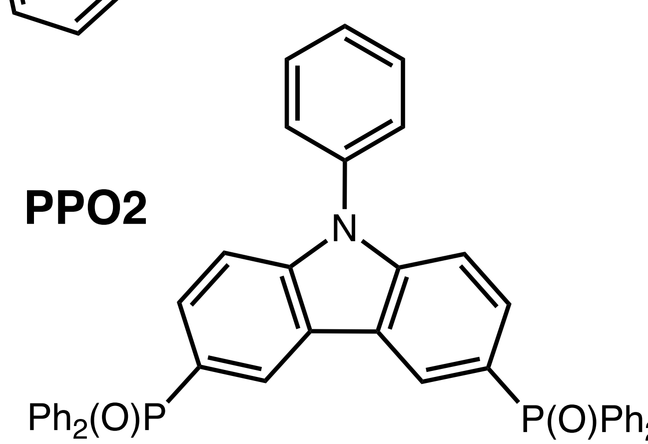


CzOXD



***m*-CZBP**

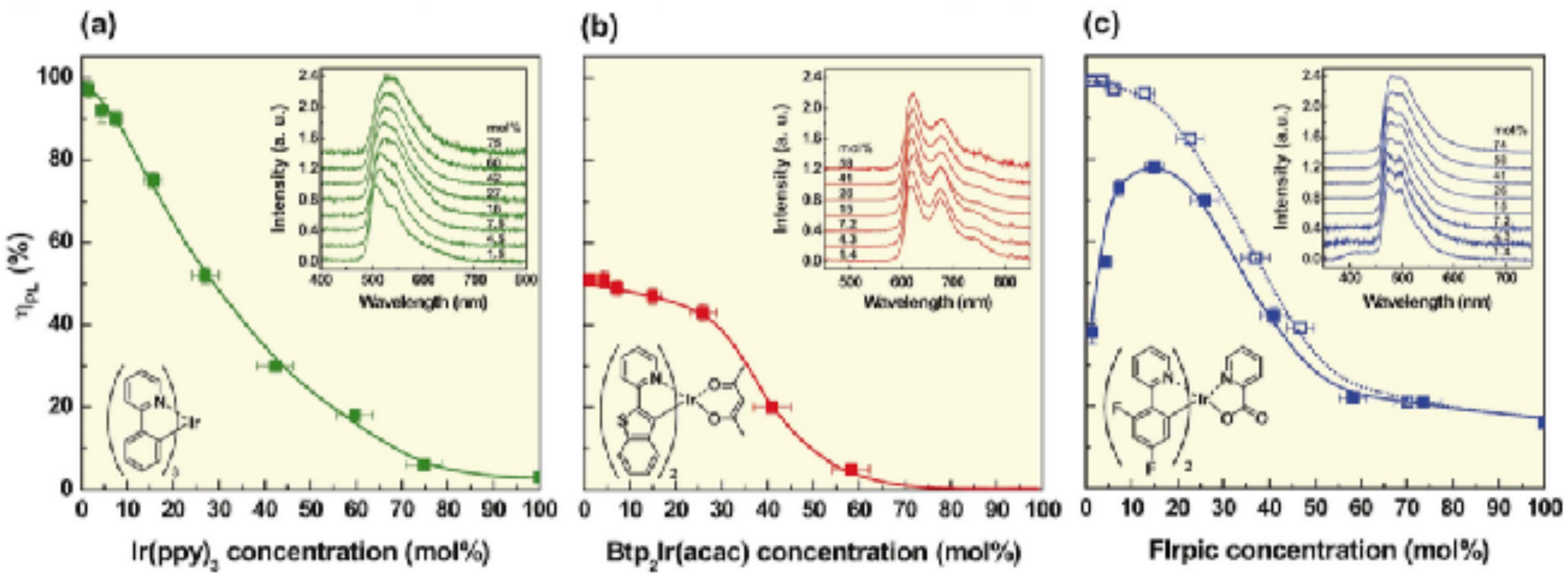
PPO2



Tao, Y.; Yang, C.; Qin, J. *Chem. Soc. Rev.* **2011**, *40*, 2943.

Dopant Concentration Effect

high concentration of dopant leads to dimished efficiency
“concentration quenching”

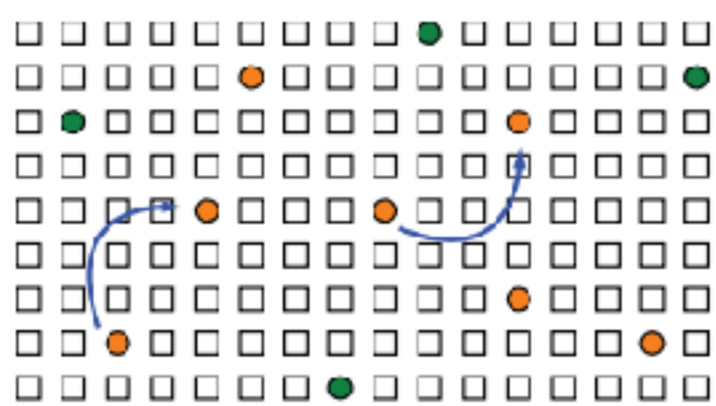


triplet-triplet annihilation

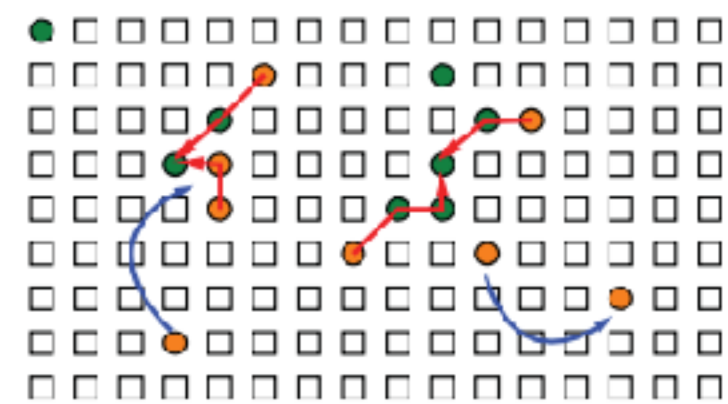
case study: Ir(ppy)$_3$ in CBP

R_F = 2.9 nm

Förster-type



Dexter-type



Staroske, W.; Pfeiffer, M.; Leo, K.; Hoffmann, M. *Phys. Rev. Lett.* ***2007****,* 98*, 197402.*
Adachi, C. *et al. Appl. Phys. Lett.* **2005**, *86*, 071104.
Reineke, S.; Baldo, M. A. *Phys. Status Solidi A* **2012**, *209*, 2341.

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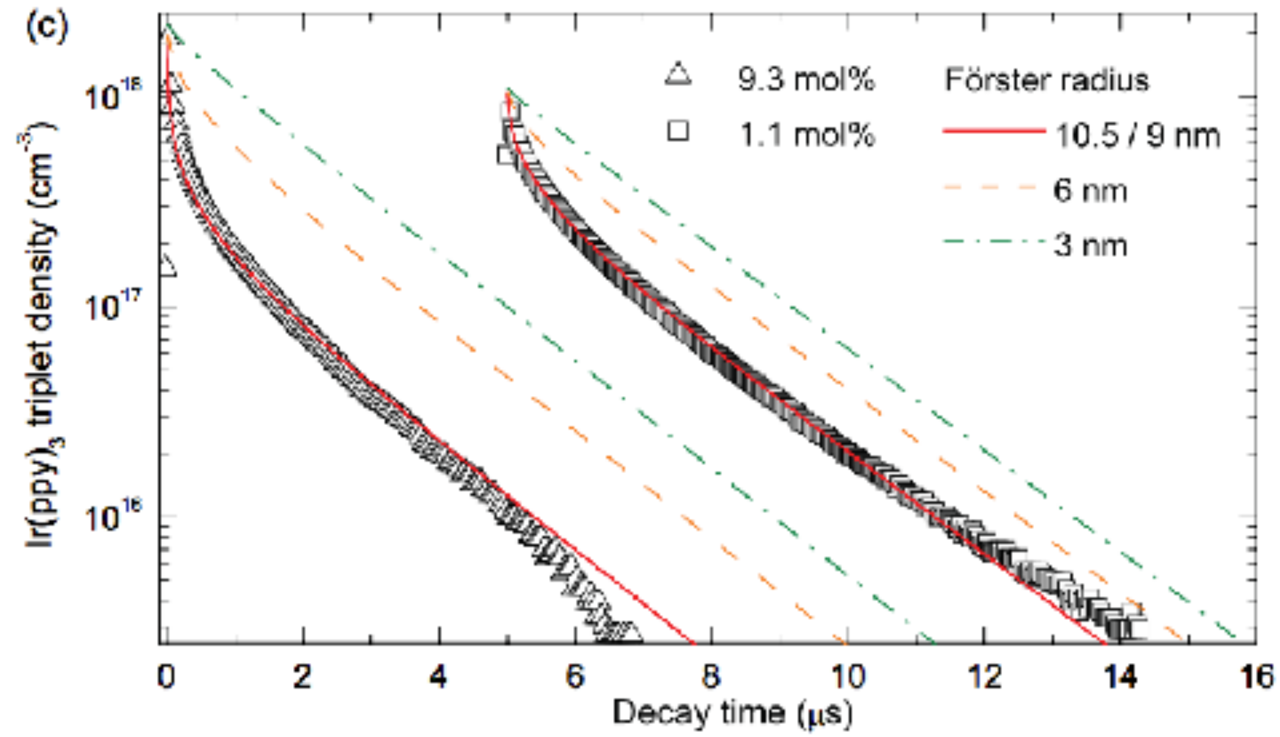
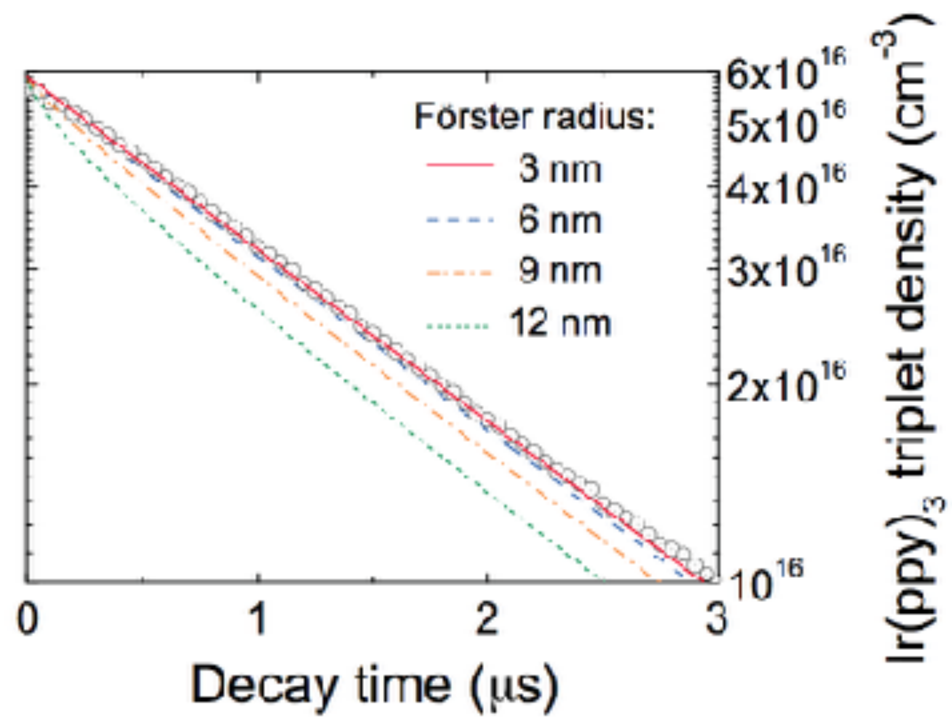


triplet-triplet annihilation

case study: $Ir(ppy)_3$ in CBP

R_F = 2.9 nm

0.1% $Ir(ppy)_3$ in TCTA



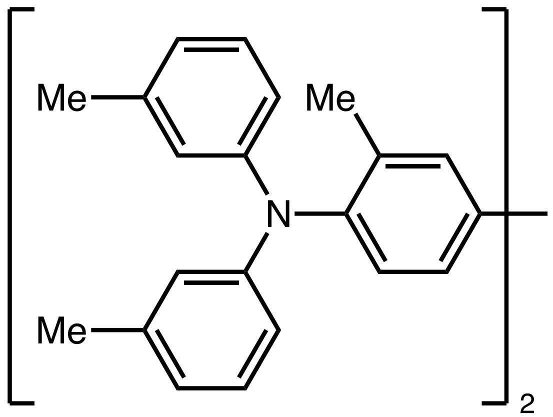
Staroske, W.; Pfeiffer, M.; Leo, K.; Hoffmann, M. *Phys. Rev. Lett.* ***2007****,* 98*, 197402.*

Adachi, C. *et al. Appl. Phys. Lett.* **2005**, *86*, 071104.

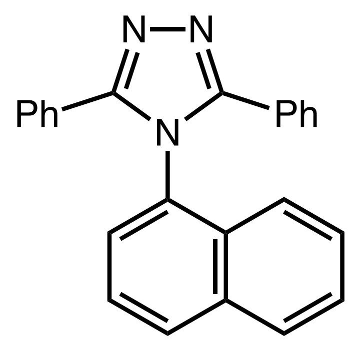
Reineke, S.; Baldo, M. A. *Phys. Status Solidi A* **2012**, *209*, 2341.

Increased IQE by Exciton Confinement

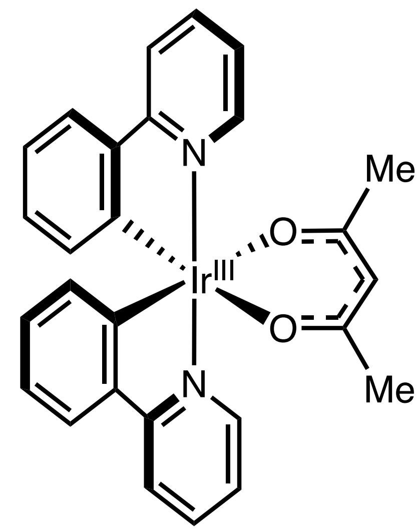
*HTL: **HMTPD***



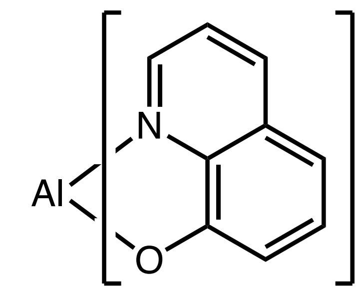
*host: **TAZ***

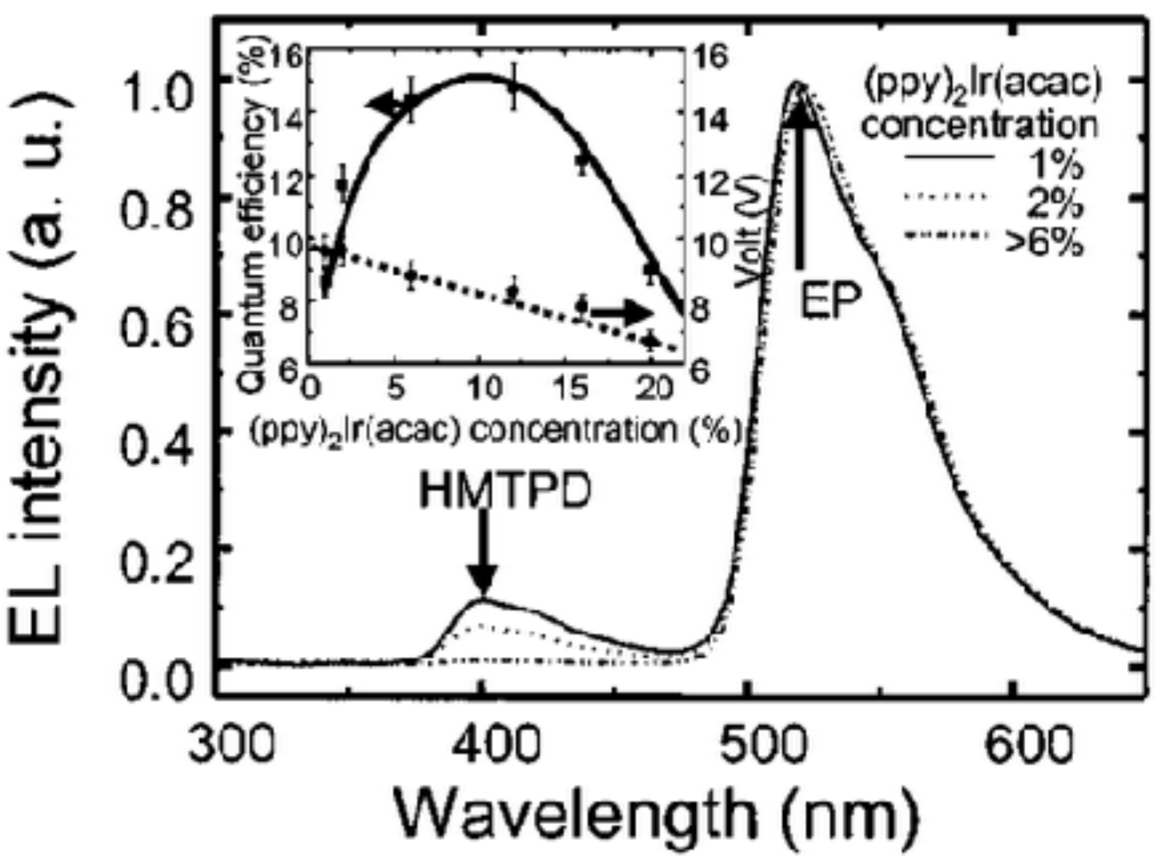


*dopant: **Ir(ppy)$_2$(acac)***



*ETL: **Alq$_3$***





emission from HMTPD likely indicates exciton formation in HTL

⇩

poor hole injection to EML/poor recombination in EML

⇩

HOMO of host is below HOMO of HTL, unfavorable hole injection

Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S R. *J. Appl. Phys.* **2001**, *90*, 5048.
Adachi, C.; Baldo, M. A.; Forrest, S R.; Thompson, M. E. *Appl. Phys. Lett.* **2000**, *77*, 904.

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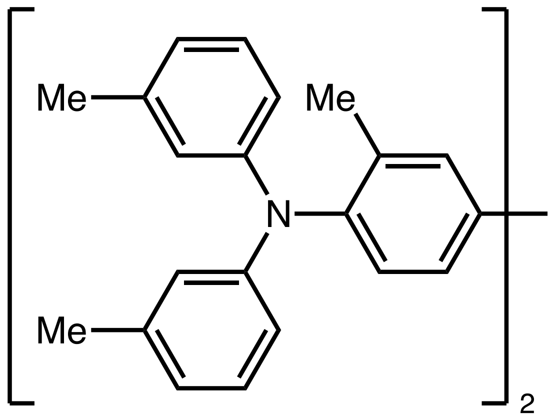
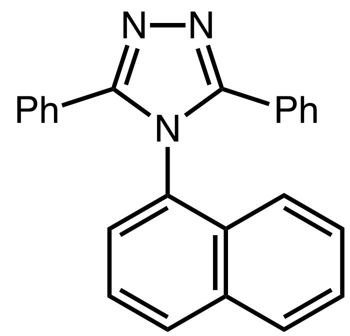
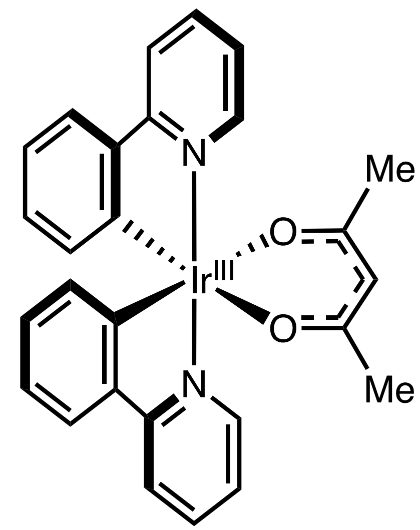


host: ***TAZ***



dopant: ***Ir(ppy)$_2$(acac)***



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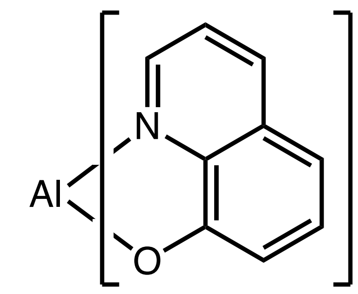

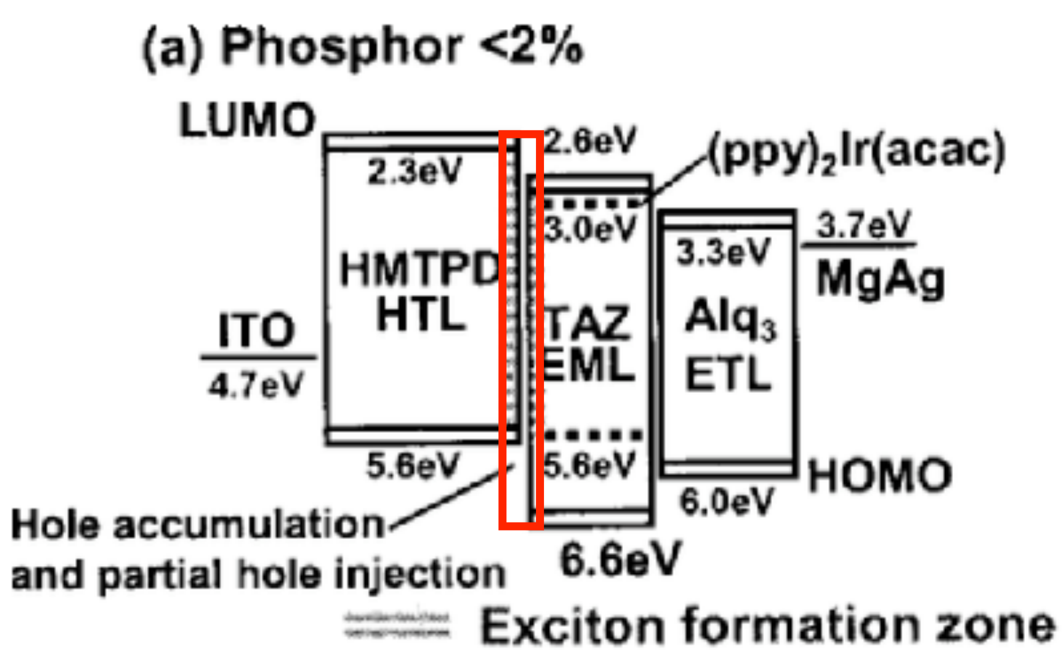

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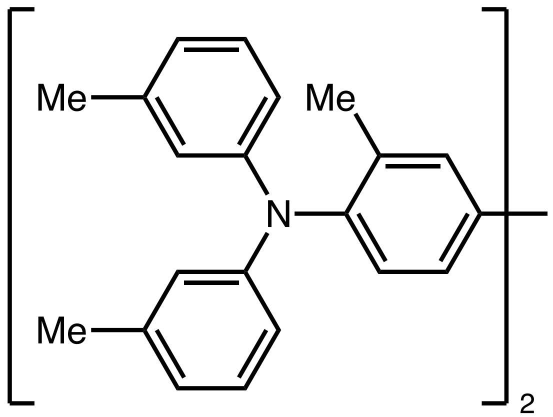
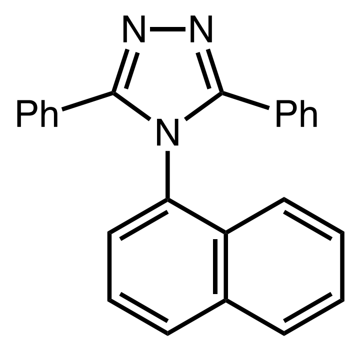


host: ***TAZ***



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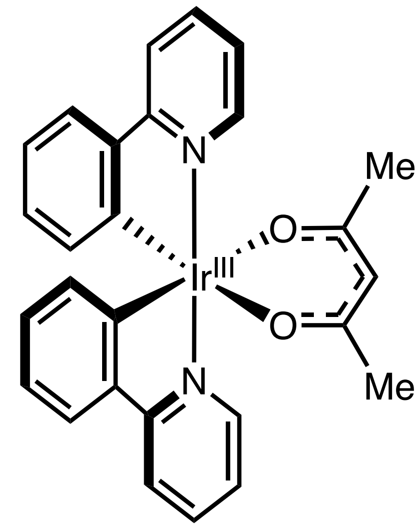
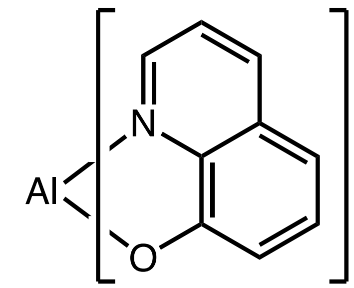
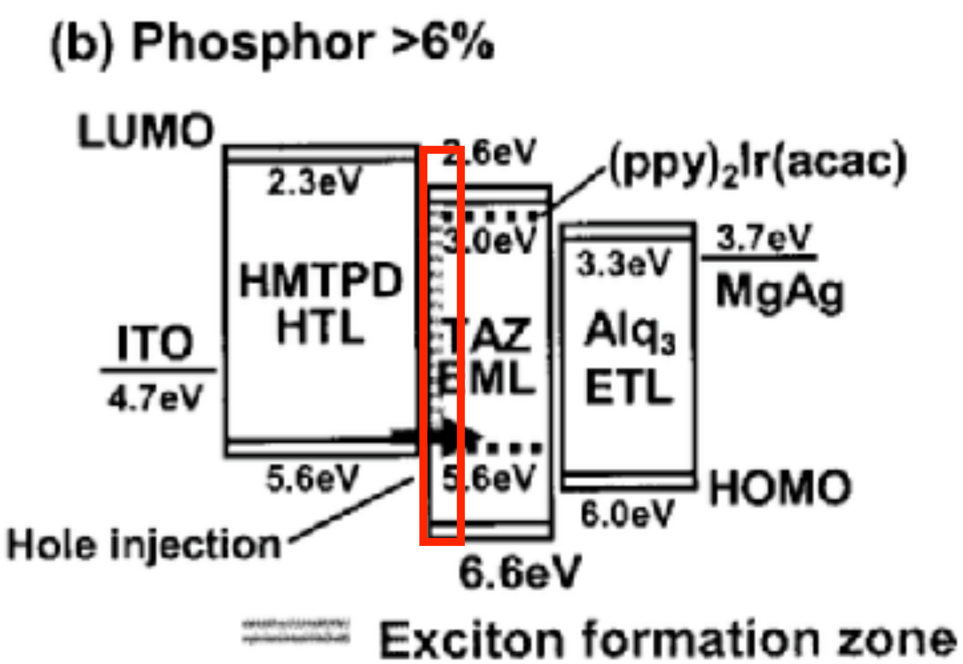


ETL: ***Alq$_3$***





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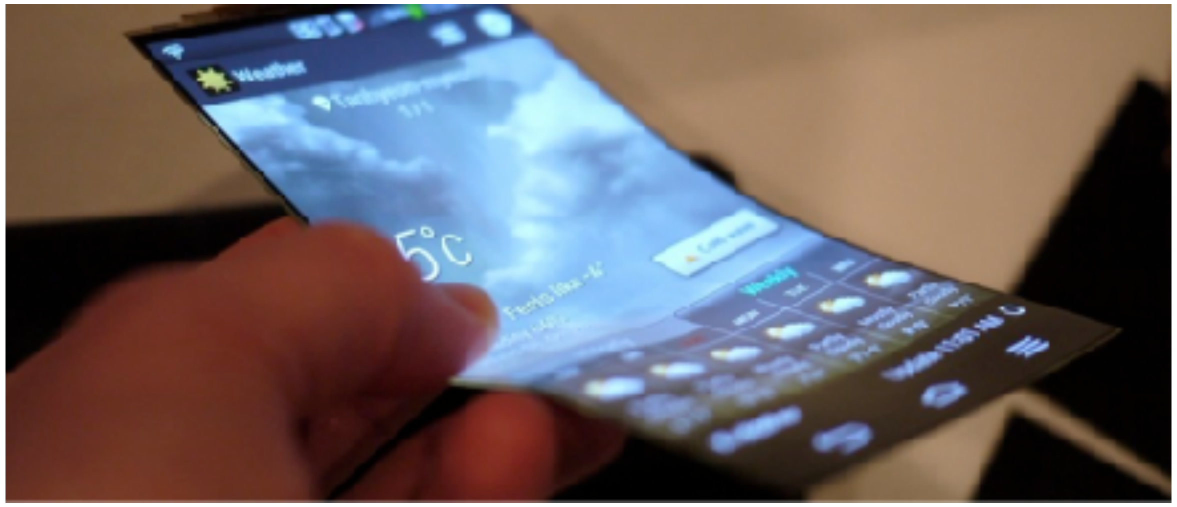
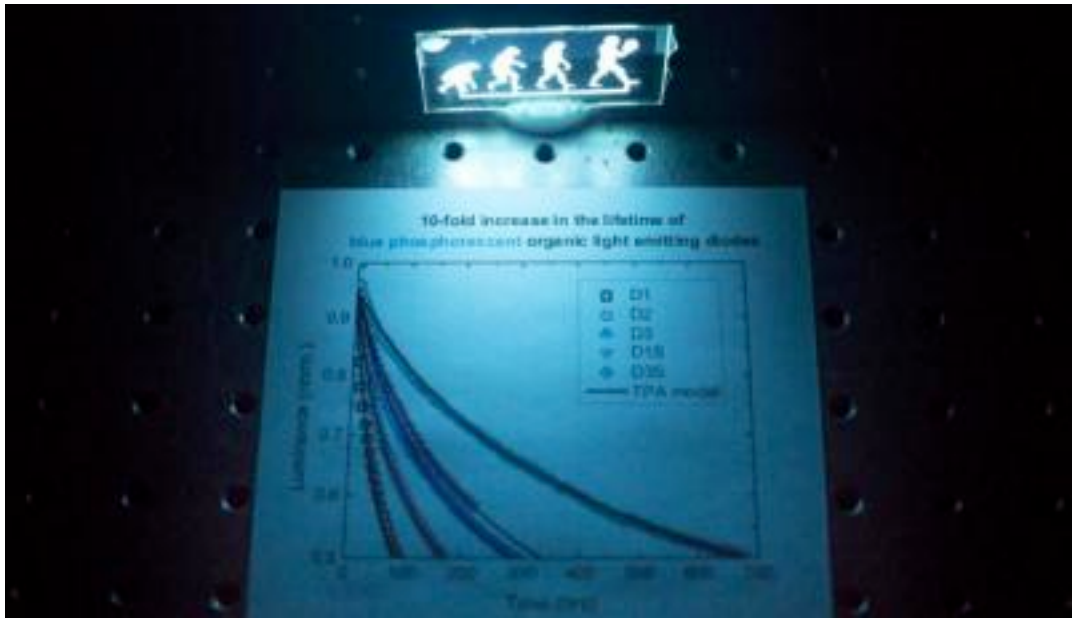
Phosphorescent OLEDs

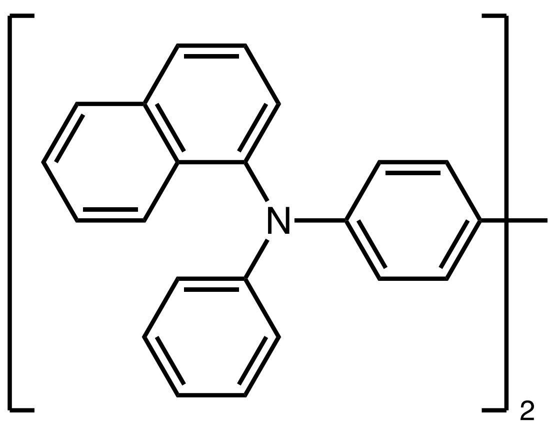
- The basics of PhOLEDs
  - Fluorescence vs. Phosphorescence
  - Basic design concept
  - Exciton formation/transfer
  - What makes a good dopant and host?
- PhOLED architectures and materials
  - Multi-layered devices
  - Phosphorescent emitters
  - Small-molecule and polymer hosts
  - Specific considerations
- Current state-of-the-art
  - Blue emitters!
  - WOLEDs via mixed fluorescence/phosphorescence
  - Thermally-activated delayed phosphorescence (TADF)



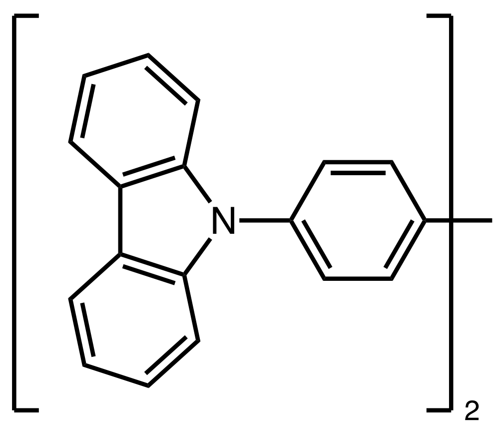


“Endothermic Energy Transfer” for Phosphorescence

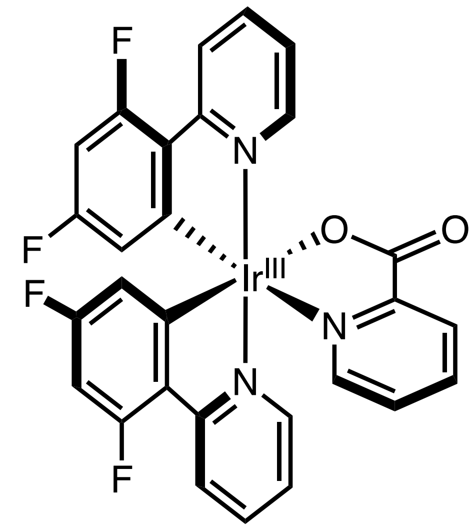
HTL: ***NPD***



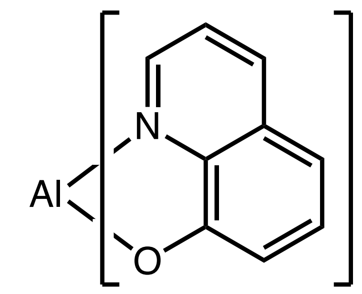
host: ***CBP***

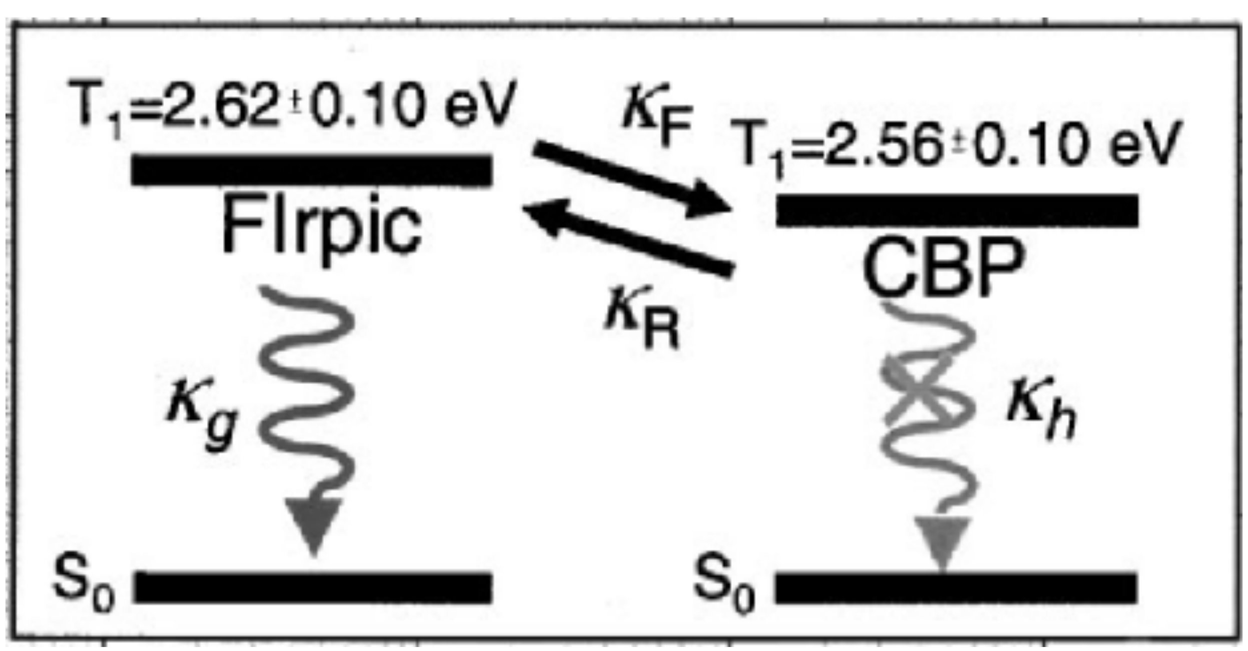


dopant: ***FIrpic***



ETL: ***Alq$_3$***





$E(T_1)$ FIrpic > $E(T_1)$ CBP
but
$k_R >> k_h$

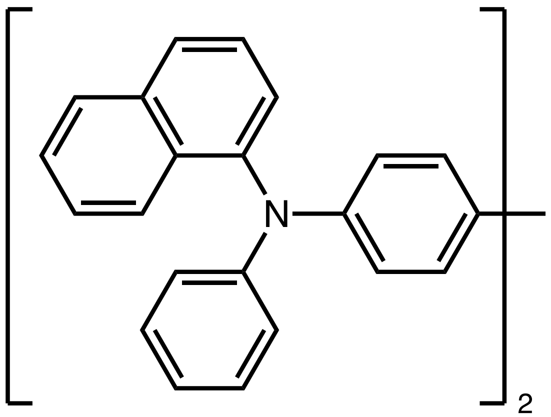
⇨

uphill ET can occur to repopulate T_1 of FIrpic leading to delayed/prolonged phosphorescence!

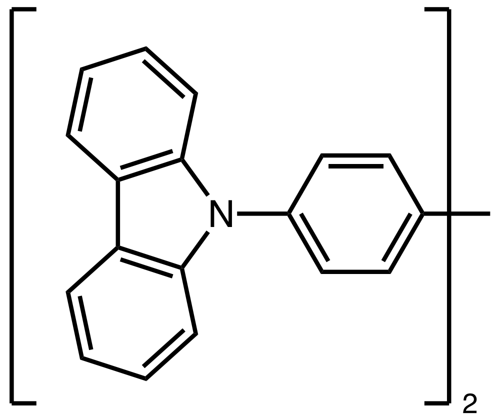
Adachi, C.; Kwong, R. C.; Djurovich, P.; Adamovich, V.; Baldo, M. A.; Thompson, M. E.; Forrest, S R. *Appl. Phys. Lett.* **2001**, *79*, 2082.

“Endothermic Energy Transfer” for Phosphorescence

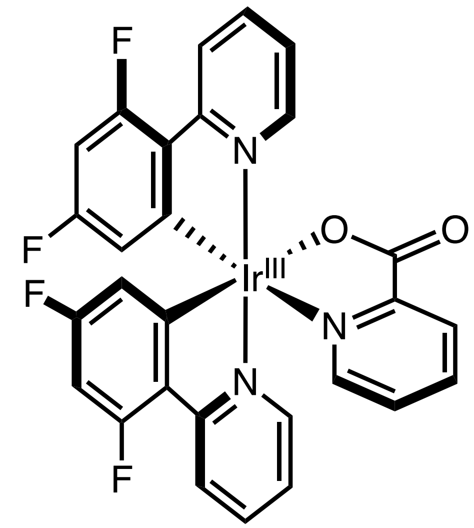
HTL: ***NPD***



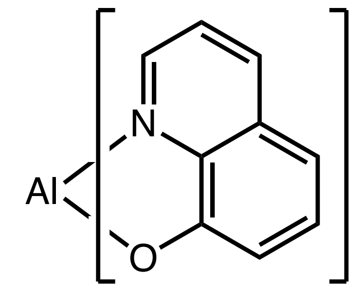
host: ***CBP***



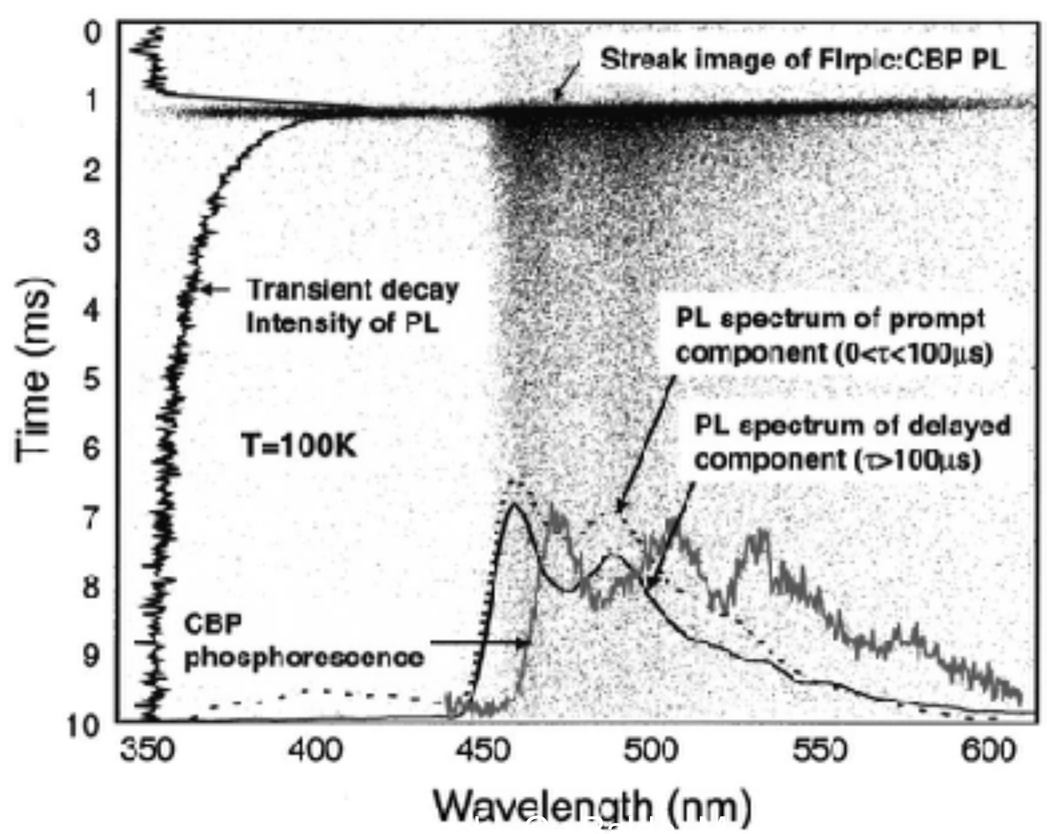
dopant: ***FIrpic***



ETL: ***Alq_3***



up to 10 ms lifetime of phosphorescence



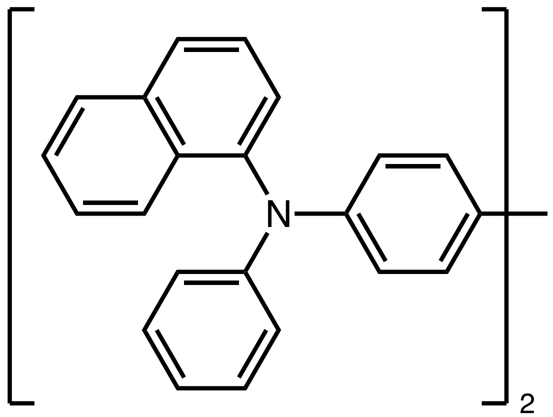
no CBP phosphorescence observed
FIrpic phosphorescence observed at both early and delayed times

$\eta_{ext} = (5.7 \pm 0.3)\%$

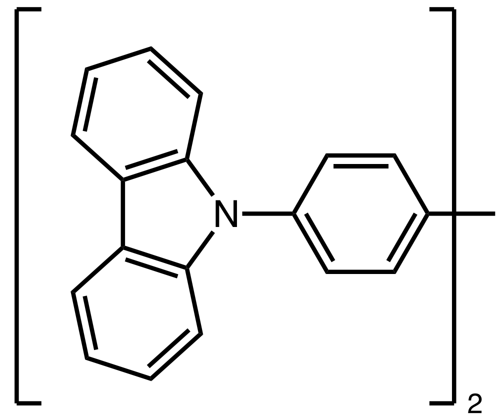
Adachi, C.; Kwong, R. C.; Djurovich, P.; Adamovich, V.; Baldo, M. A.; Thompson, M. E.; Forrest, S R. *Appl. Phys. Lett.* **2001**, *79*, 2082.

Improved Efficiency in Blue Phosphorescent LEDs

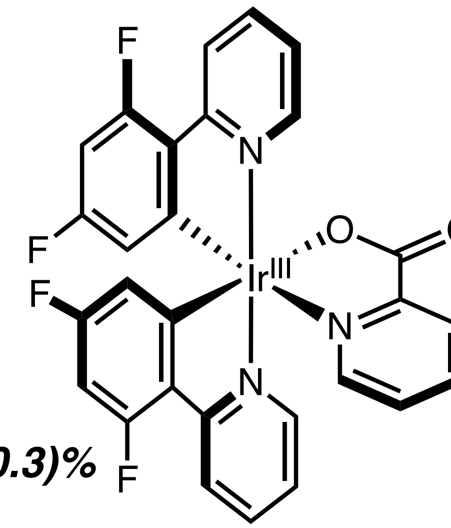
HTL: ***NPD***



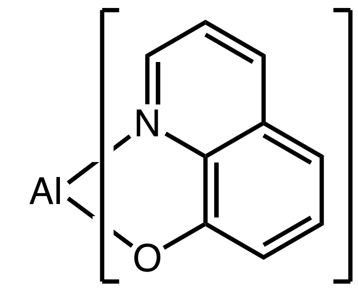
host: ***CBP***



dopant: ***FIrpic***



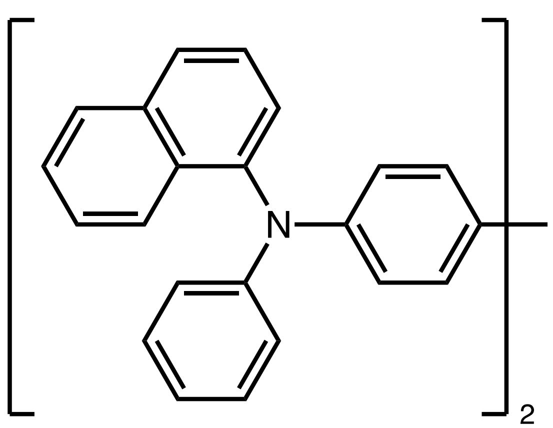
ETL: ***Alq$_3$***



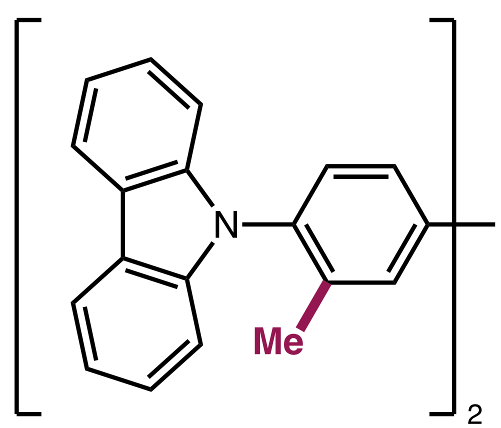
η_{ext} = (5.7±0.3)%

η_{ext} = 10.4%

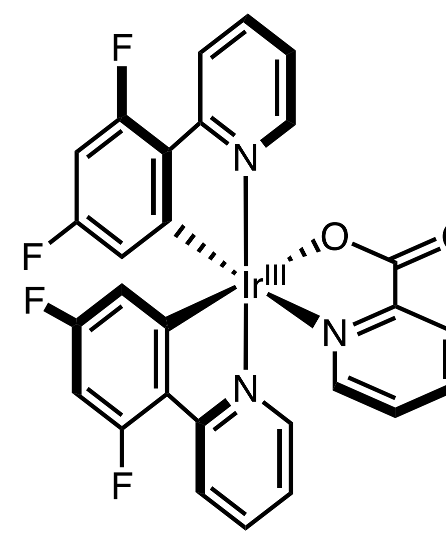
HTL: ***NPD***



host: ***CDBP***



dopant: ***FIrpic***



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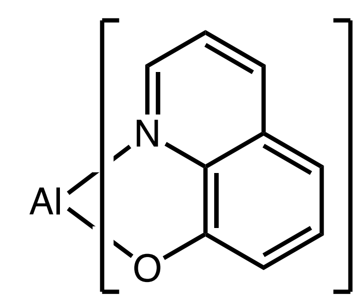

Tokito, S.; Ijima, T.; Suzuri, Y.; Kita, H.; Tsuzuki, T.; Sato, F. *Appl. Phys. Lett.* **2003**, *83*, 569.
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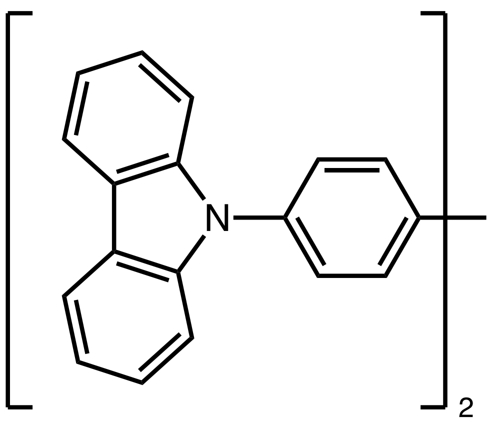
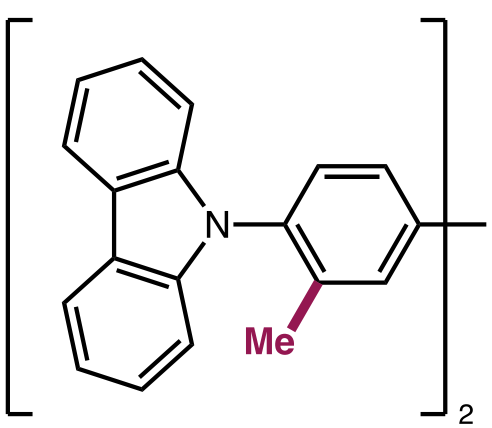
Improved Efficiency in Blue Phosphorescent LEDs

host: ***CBP***



η_{ext} = (5.7±0.3)%

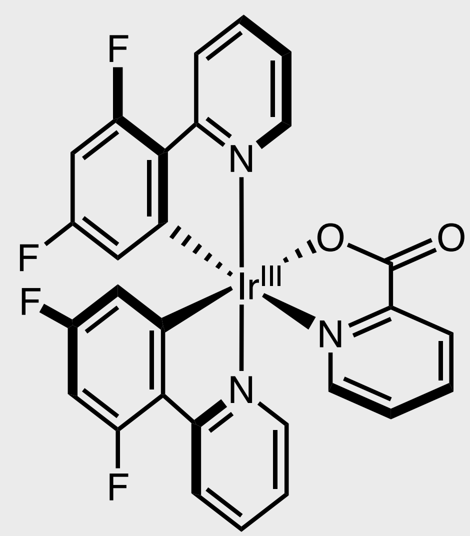
host: ***CDBP***



η_{ext} = 10.4%

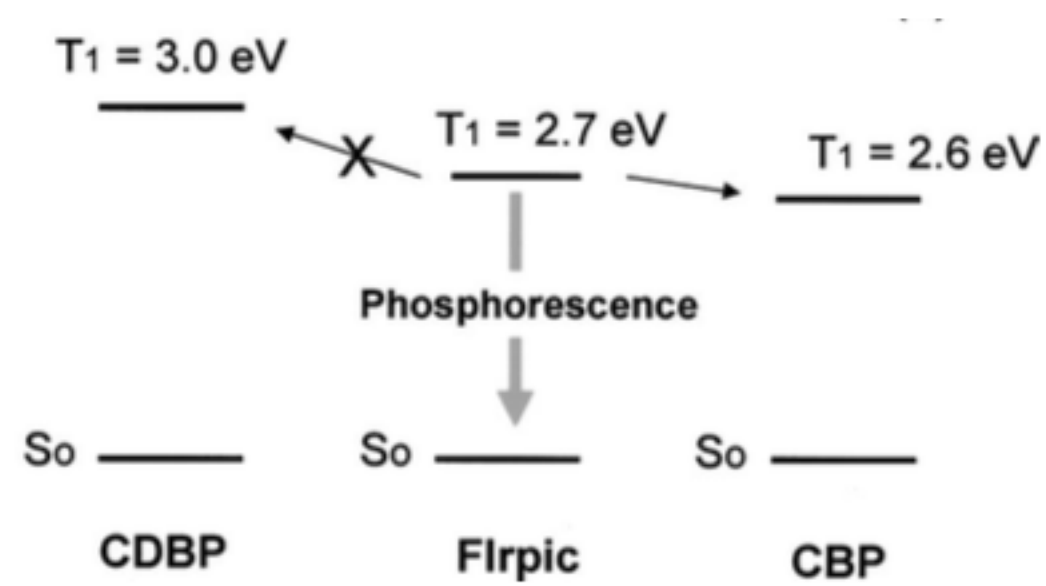
E(T$_1$) = 2.6 eV

dopant: ***FIrpic***



E(T$_1$) = 3.0 eV

exothermic ET to phosphor is
more efficient than endothermic



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Improved Efficiency in Blue Phosphorescent LEDs

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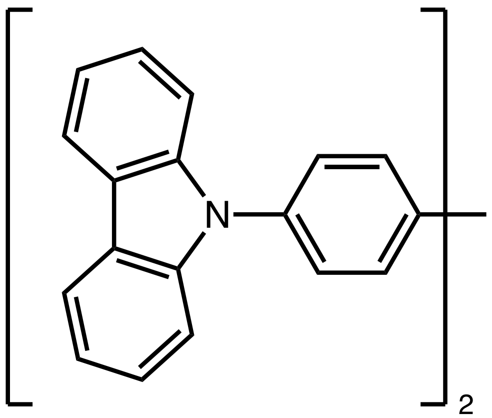

η_{ext} = (5.7±0.3)%

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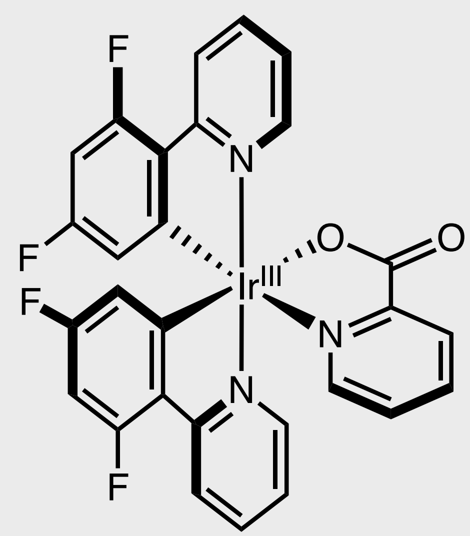
dopant: ***FIrpic***



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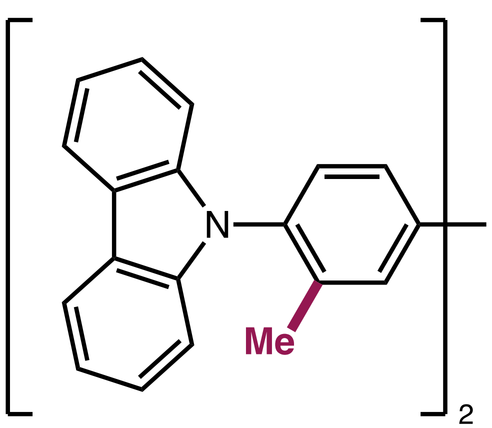

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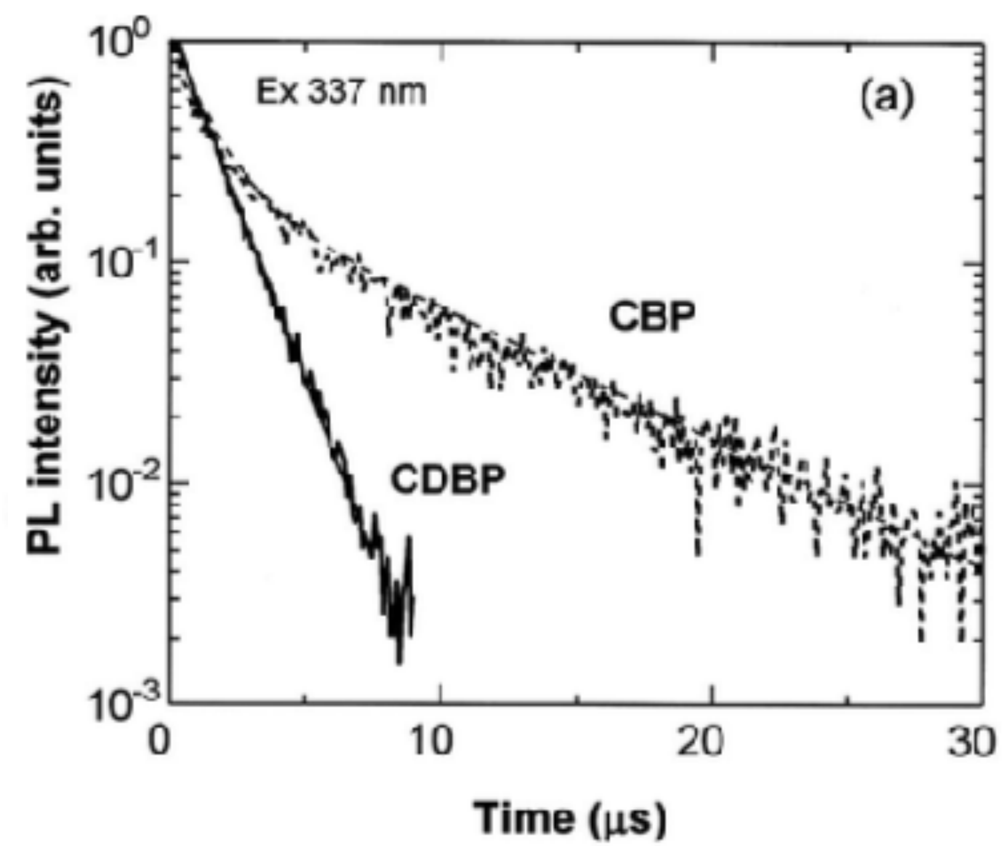
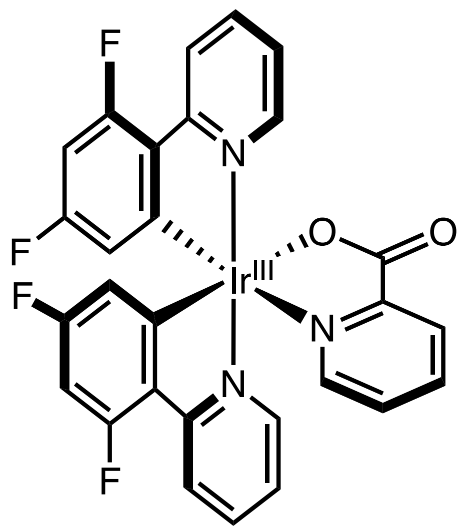


phosphorescence decays
significantly faster

Tokito, S.; Ijima, T.; Suzuri, Y.; Kita, H.; Tsuzuki, T.; Sato, F. *Appl. Phys. Lett.* **2003**, *83*, 569.
Adachi, C.; Kwong, R. C.; Djurovich, P.; Adamovich, V.; Baldo, M. A.; Thompson, M. E.; Forrest, S R. *Appl. Phys. Lett.* **2001**, *79*, 2082.

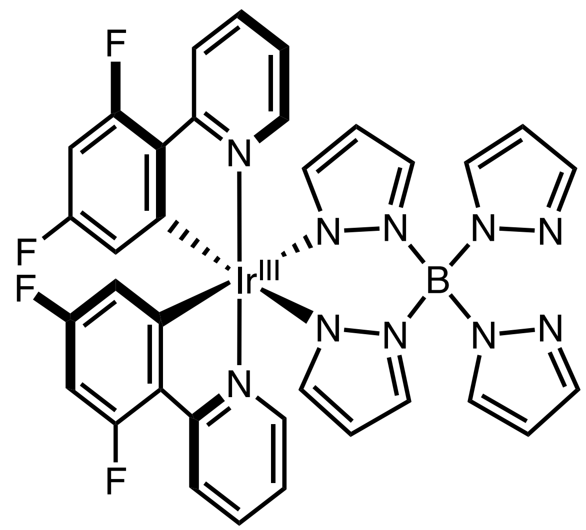
Improving Stability and Lifetime of Blue PhOLEDs



FIrpic

λ_{max} = 476 nm

T_1 lifetime = 1.2 μs

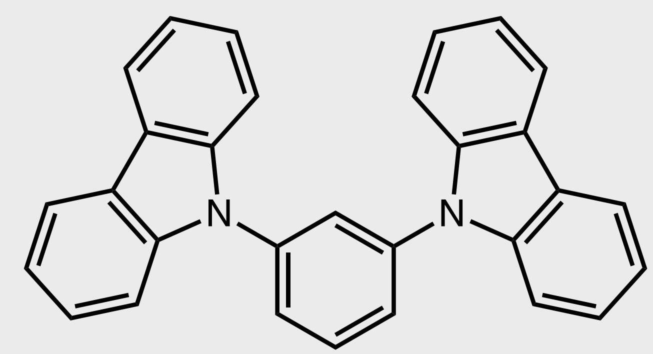


FIr6

λ_{max} = 458 nm

T_1 lifetime = 2.2 μs

as films in mCP



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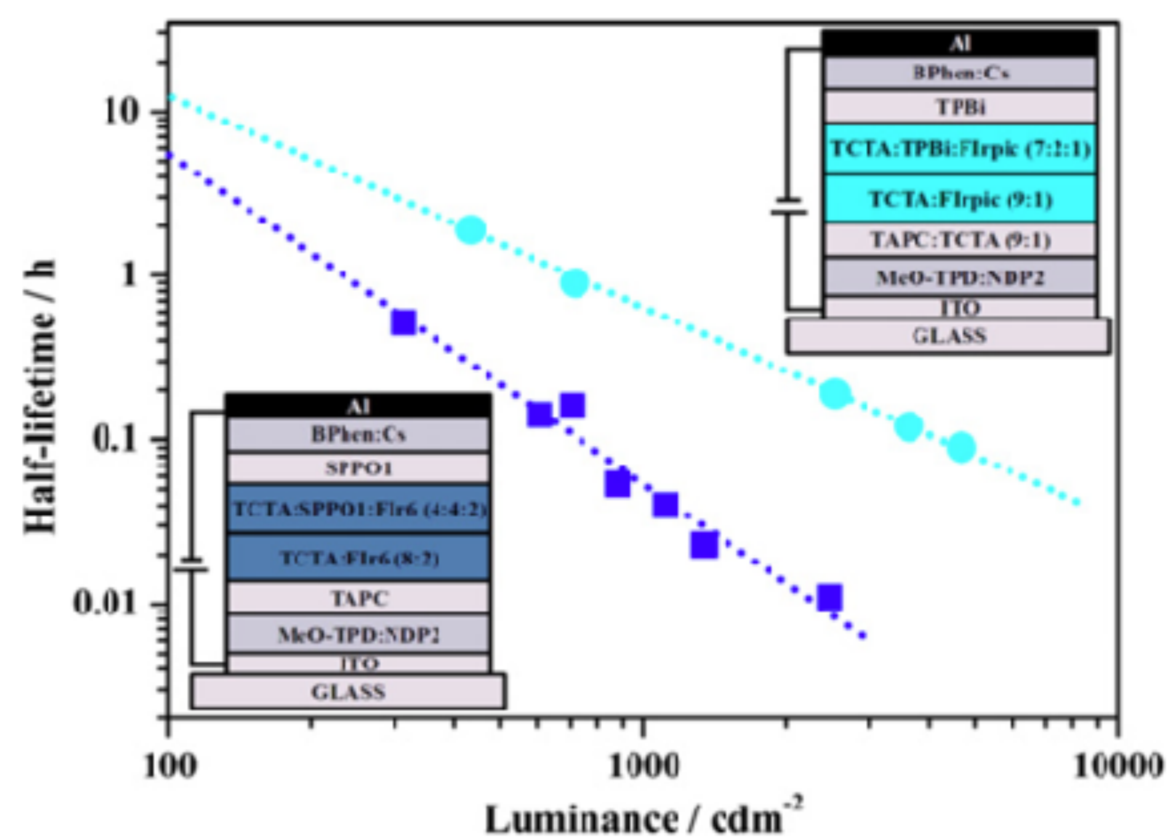
high triplet energy emitters

rapid decay of pure films and OLED devices

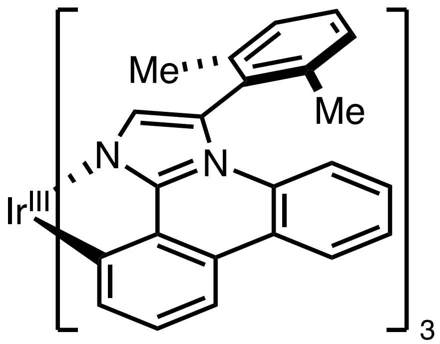
stabilization with improved hosts, HBL, etc



Endo, A.; Suzuki, K.; Yoshihara, T.; Tobita, S.; Yahiro, M.; Adachi, C. *Chem. Phys. Lett.* **2008**, *460*, 155.

Seifert, R.; Rabelo de Moraes, I.; Scholz, S.; Gather, M. C.; Lussem, B.; Leo, K. *Org. Electron.* **2013**, *14*, 115.

Improving Stability and Lifetime of Blue PhOLEDs

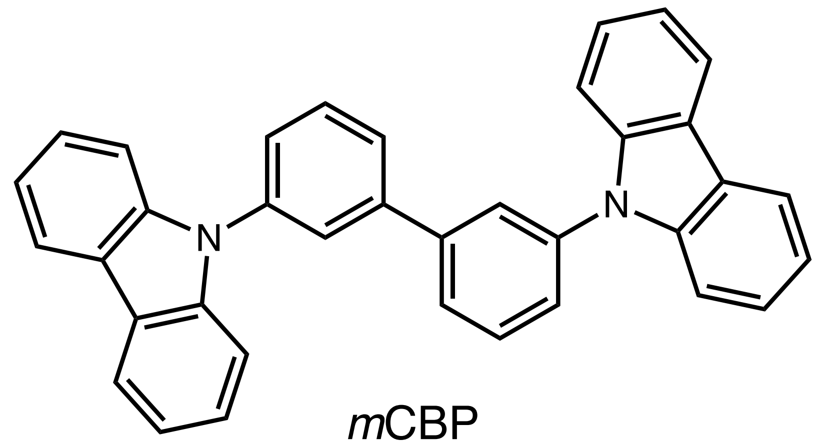


Ir(dmp)$_3$

λ_{max} = 466 nm

E(HOMO) = 5.0 eV

hole transport in EML

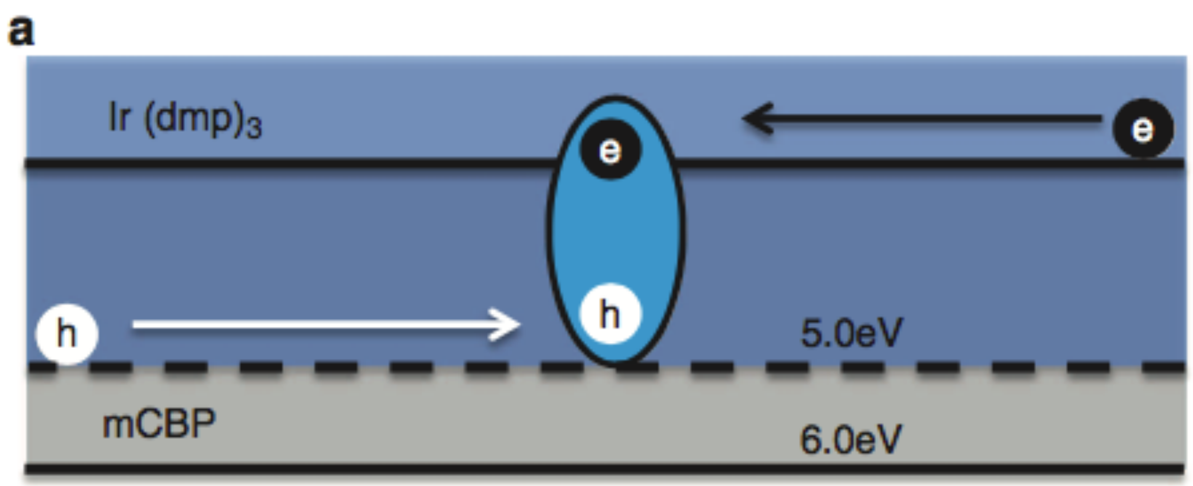


*m*CBP

E(HOMO) = 6.0 eV

electron transport in EML

⇨ *at high Ir(dmp)$_3$ concentrations, exciton formation should occur only in vicinty of/on Ir(dmp)$_3$*



Zhang, Y.; Lee, J.; Forrest, S. R. *Nat. Commun.* **2014**, *5*, 5008.

Seifert, R.; Rabelo de Moraes, I.; Scholz, S.; Gather, M. C.; Lussem, B.; Leo, K. *Org. Electron.* **2013**, *14*, 115.

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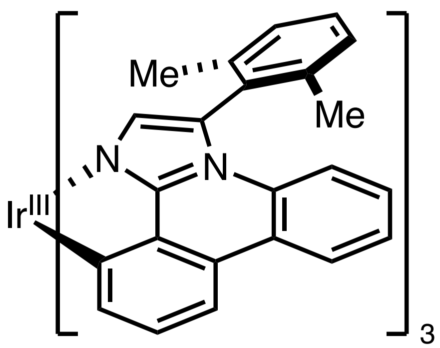
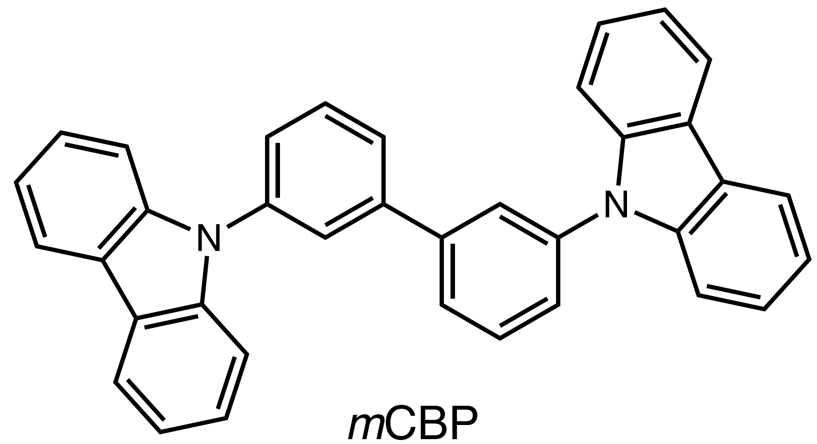


$Ir(dmp)_3$
λ_{max} = 466 nm
E(HOMO) = 5.0 eV
hole transport in EML

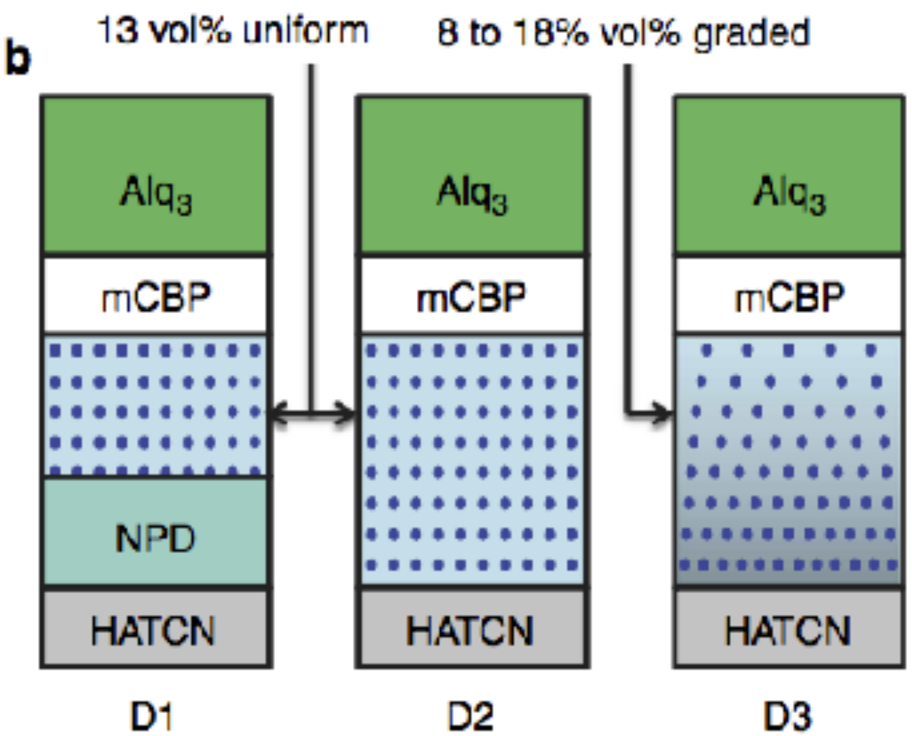


*m*CBP

E(HOMO) = 6.0 eV

electron transport in EML

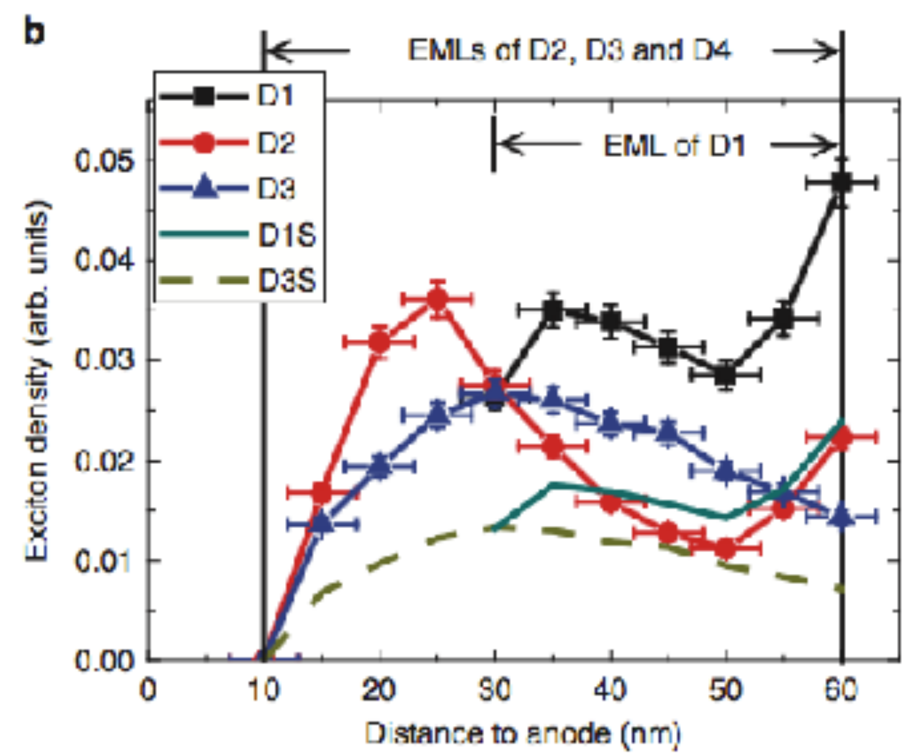
at high $Ir(dmp)_3$ concentrations, exciton formation should occur only in vicinty of/on $Ir(dmp)_3$



anode

η_{ext}= (8.5±0.1)%
T50 = 510 h

η_{ext} = (9.5±0.1)%
T50 = 1500-1600 h



Zhang, Y.; Lee, J.; Forrest, S. R. *Nat. Commun.* **2014**, *5*, 5008.
Seifert, R.; Rabelo de Moraes, I.; Scholz, S.; Gather, M. C.; Lussem, B.; Leo, K. *Org. Electron.* **2013**, *14*, 115.

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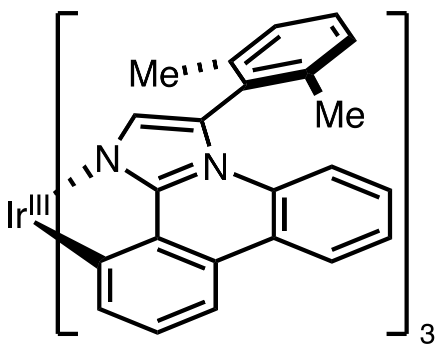
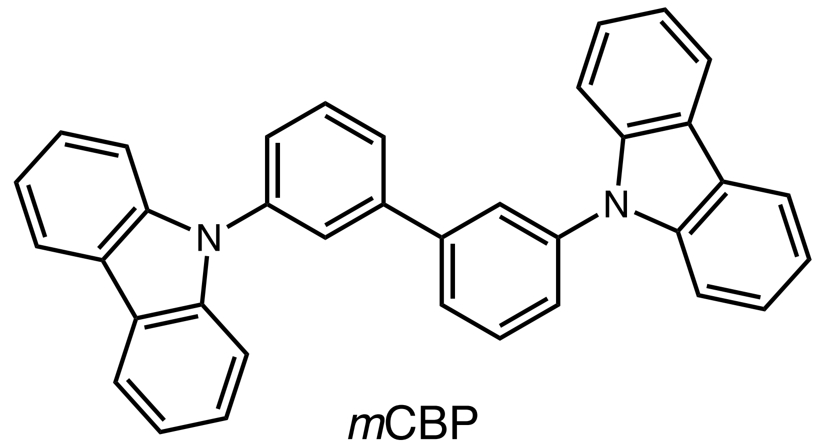


Ir(dmp)$_3$
λ_{max} = 466 nm
E(HOMO) = 5.0 eV
hole transport in EML

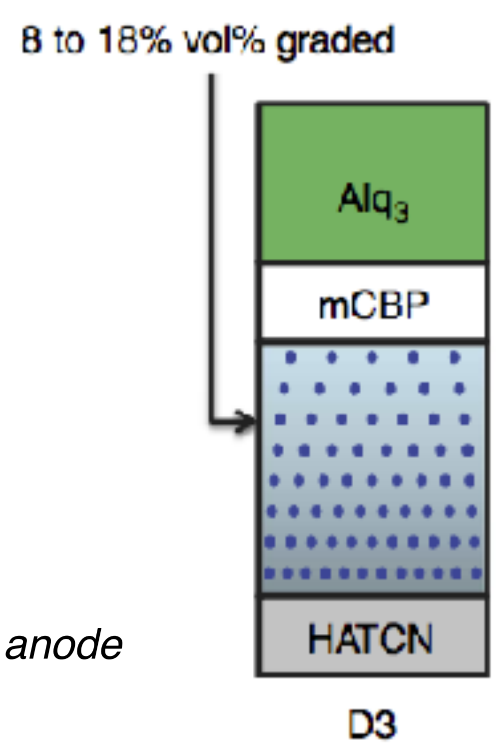


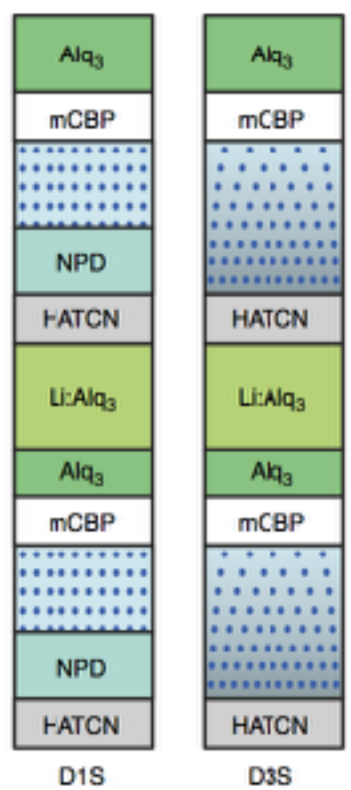
*m*CBP

E(HOMO) = 6.0 eV
electron transport in EML

⇨ *at high Ir(dmp)$_3$ concentrations, exciton formation should occur only in vicinty of/on Ir(dmp)$_3$*

anode

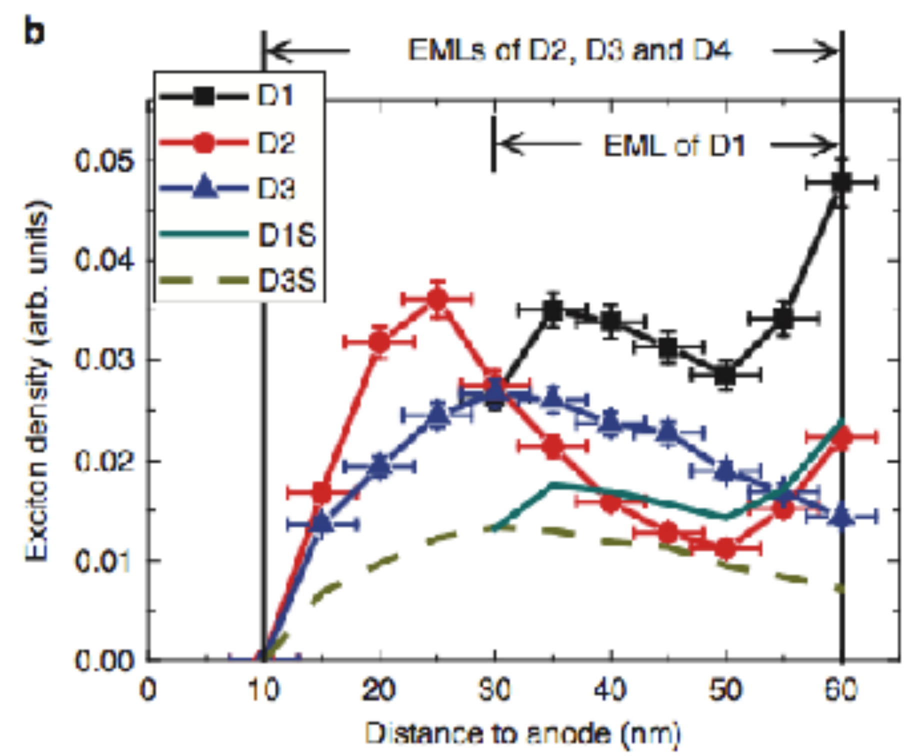




η_{ext} = (9.5±0.1)%
T50 = 1500-1600 h

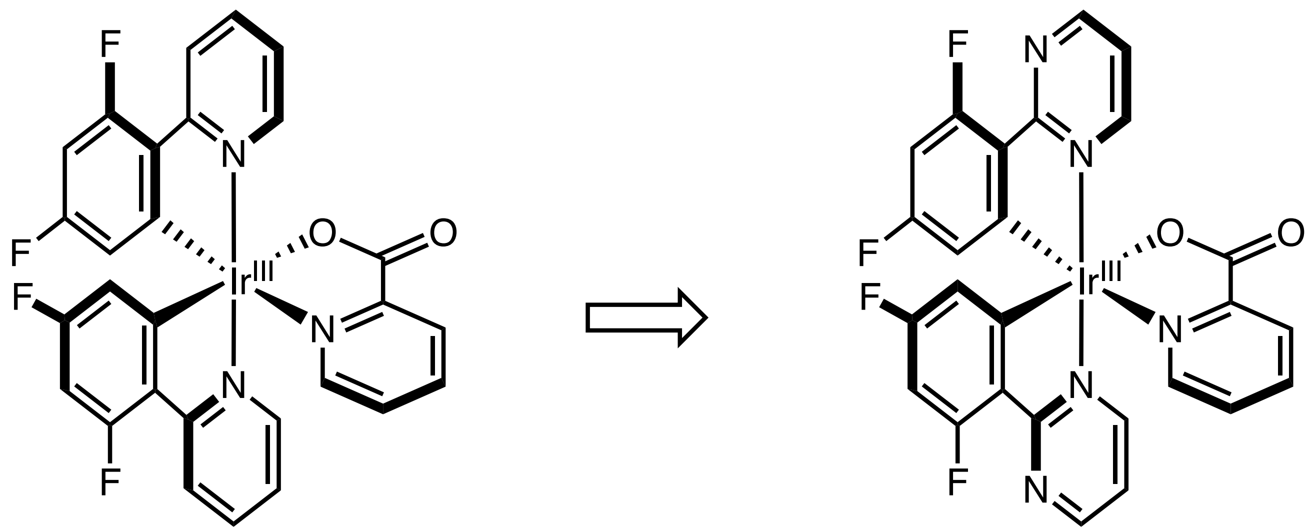
η_{ext} = (18±0.2)%
T50 = 3500-3700 h

⇨



Zhang, Y.; Lee, J.; Forrest, S. R. *Nat. Commun.* **2014**, *5*, 5008.
Seifert, R.; Rabelo de Moraes, I.; Scholz, S.; Gather, M. C.; Lussem, B.; Leo, K. *Org. Electron.* **2013**, *14*, 115.

Improving Stability and Lifetime of Blue PhOLEDs



FIrpic

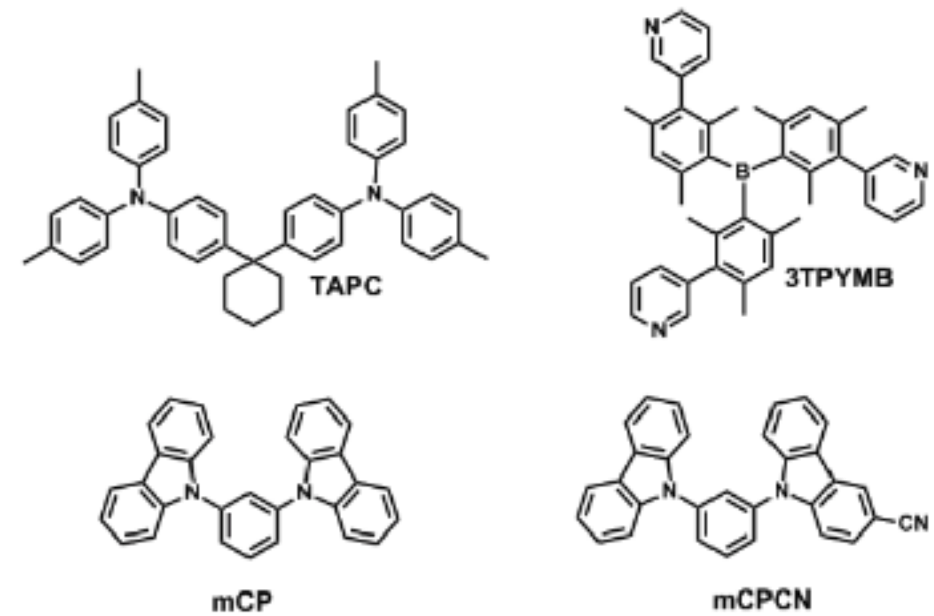
λ_{max} = 470 nm

T_1 lifetime = 1.1 μs

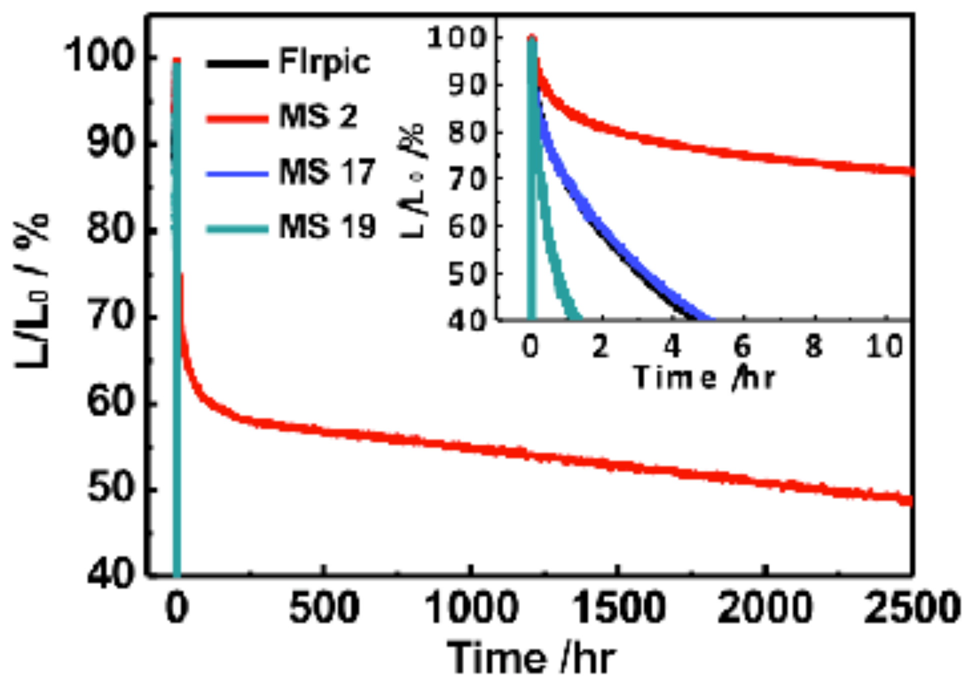
MS2

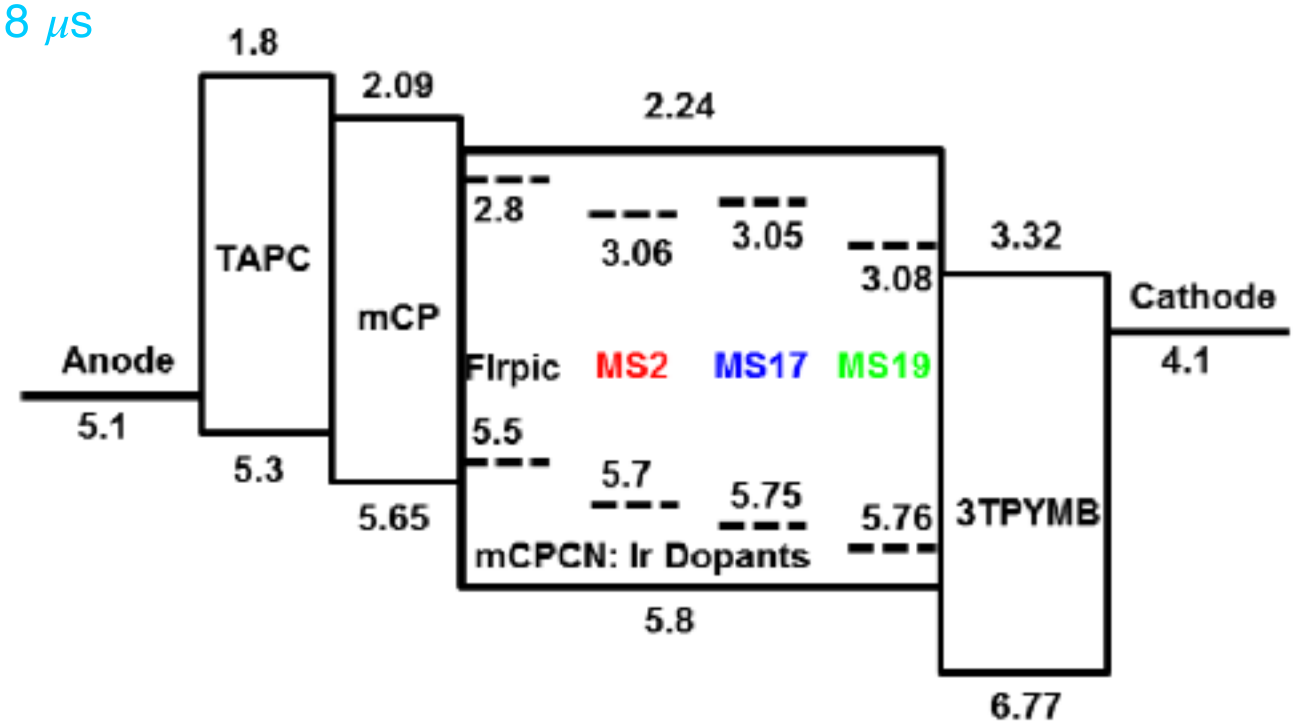
λ_{max} = 475 nm

T_1 lifetime = 0.8 μs



A

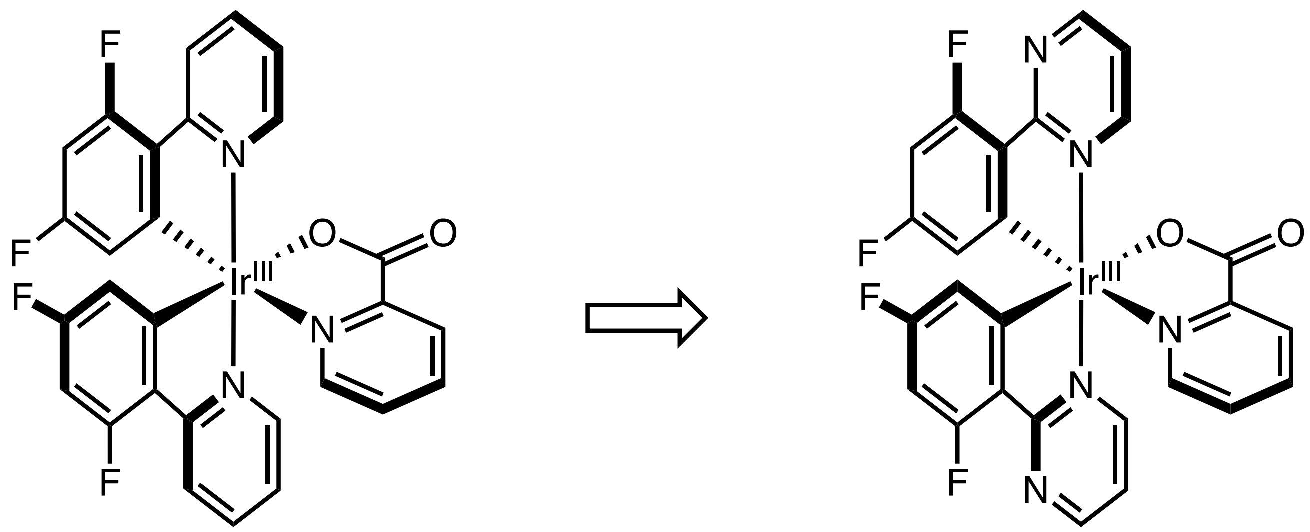




B

Sarma, M.; Tsai, W.-L.; Lee, W.-K.; Chi, Y.; Wu, C.-C.; Liu, S.-H.; Chou, P.-T.; Wong, K.-T. *Chem* **2017**, *3*, 461.

Improving Stability and Lifetime of Blue PhOLEDs



FIrpic

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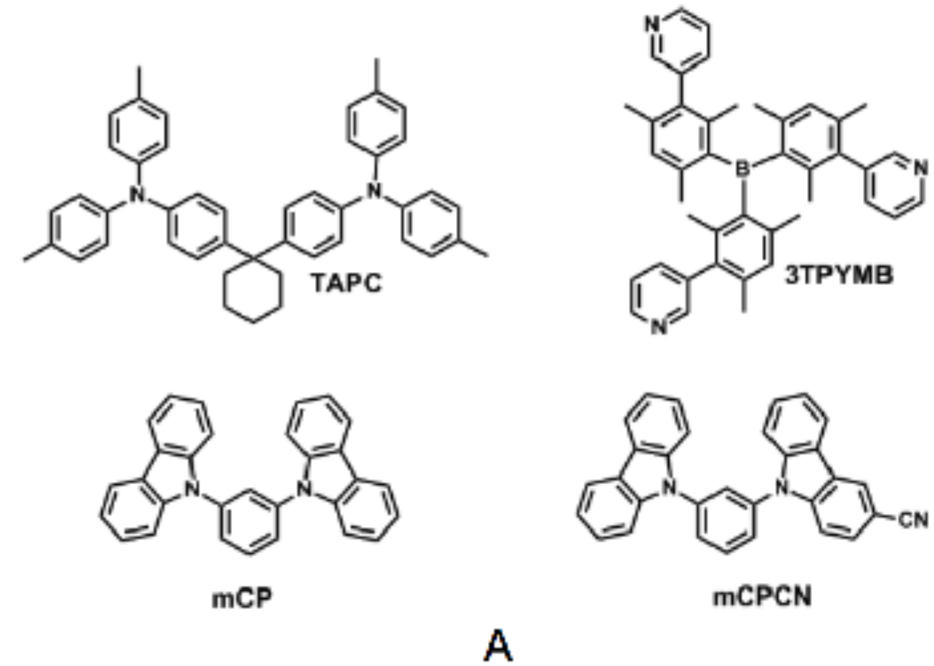
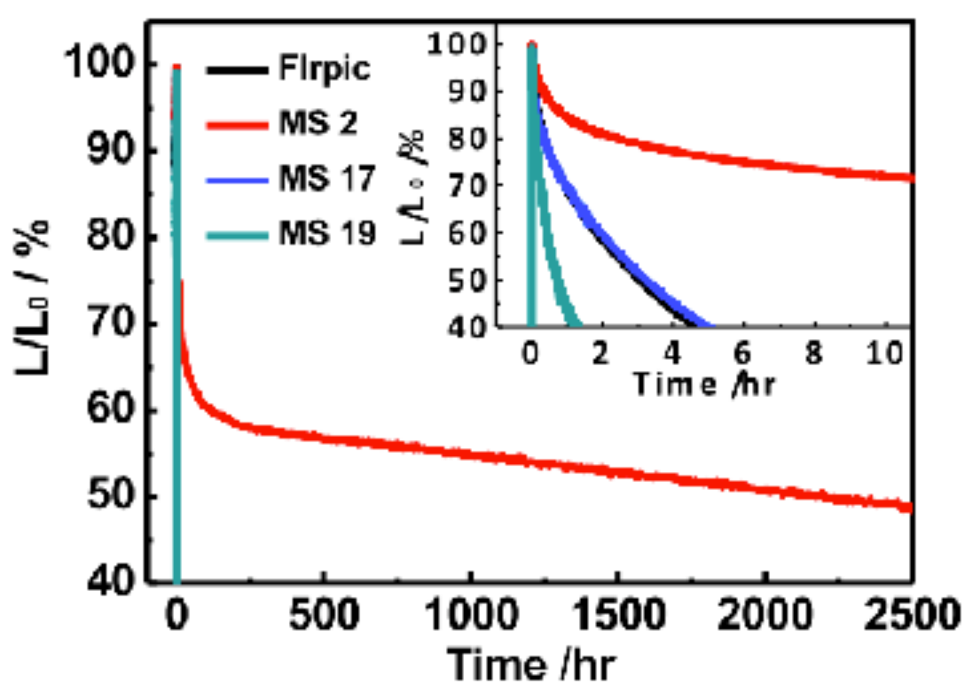
T_1 lifetime = 1.1 μs

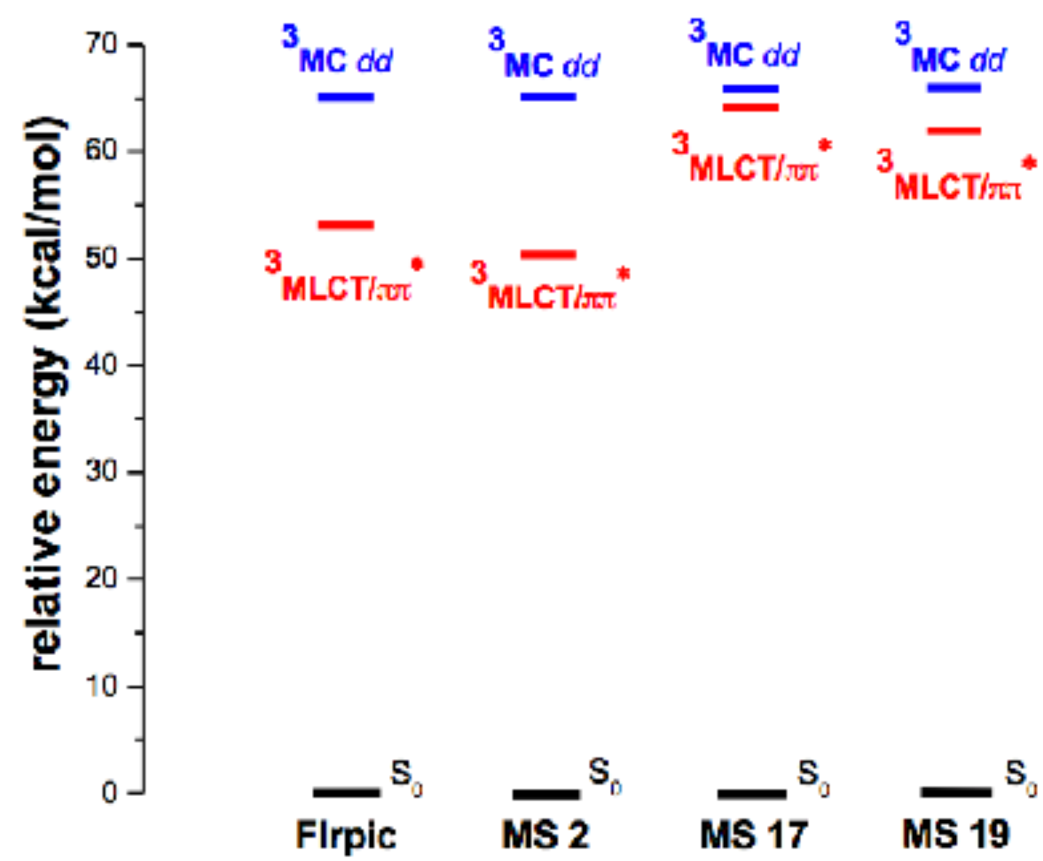
MS2

λ_{max} = 475 nm

T_1 lifetime = 0.8 μs



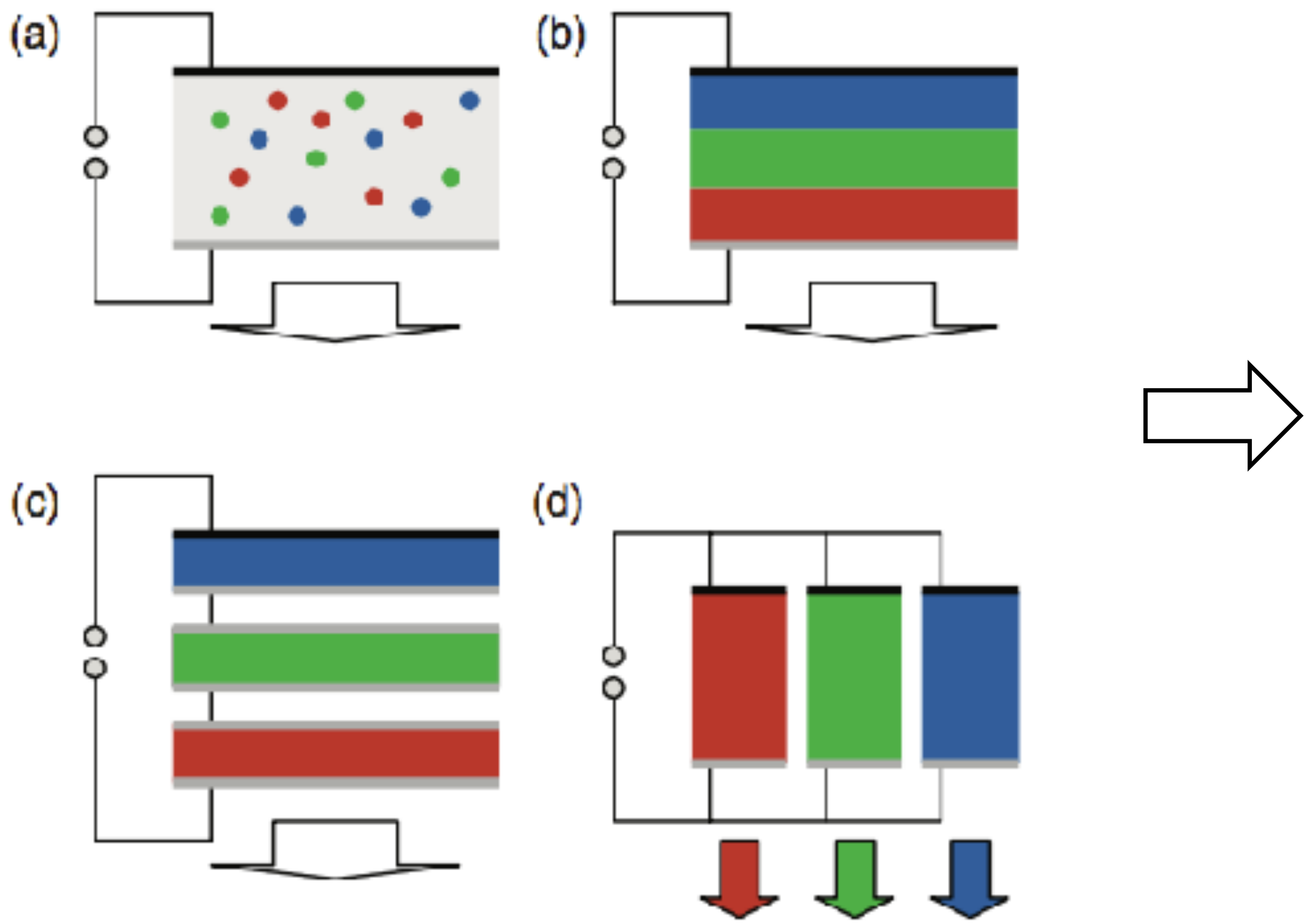




Sarma, M.; Tsai, W.-L.; Lee, W.-K.; Chi, Y.; Wu, C.-C.; Liu, S.-H.; Chou, P.-T.; Wong, K.-T. *Chem* **2017**, *3*, 461.

White OLEDs (WOLEDs)

white light = blended blue, green, red



Red PhOLED ✓

Green PhOLED ✓

Blue PhOLED ?

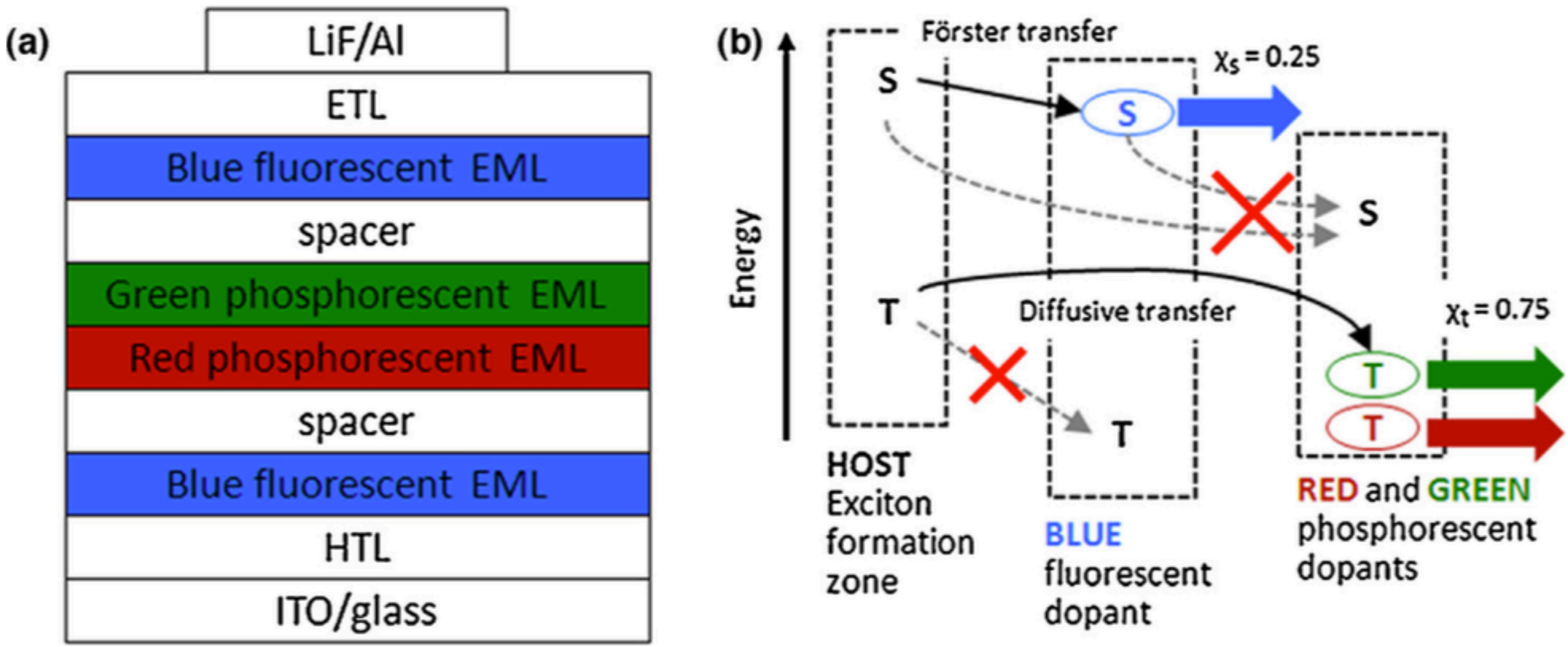
Solution: combine blue fluorescence with red/green phosphorescence

Gather, M. C.; Köhnen, A.; Meerholz, K. *Adv. Mater.* **2011**, *23*, 233.

White OLEDs (WOLEDs)

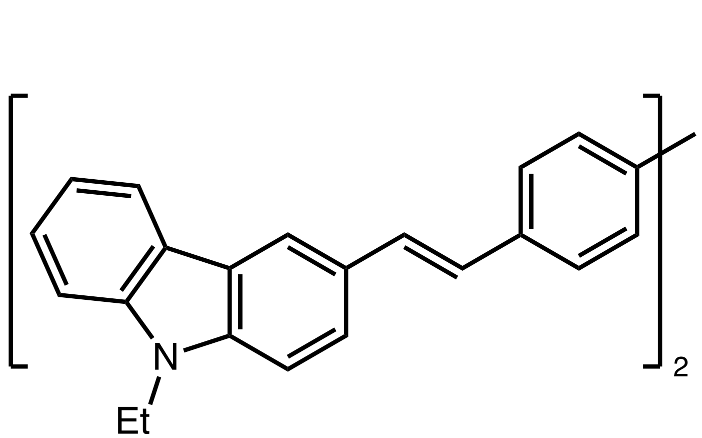
Working principle:

trap singlets on blue flourescent emitter
trap triplets on red/green phosphorescent emitter

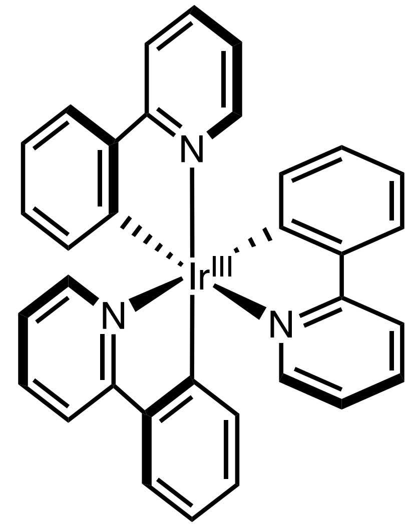


Chen, J.; Zhao, F.; Ma, D. *Mater. Today* **2014**, *17*, 175.
Sun, Y.; Biebink, N. C.; Kanno, H.; Ma, B.; Thompson, M. E.; Forrest, S. R. *Nature* **2006**, *440*, 908.

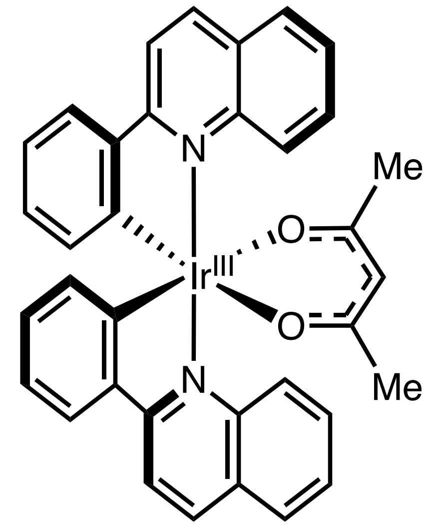
White OLEDs (WOLEDs)



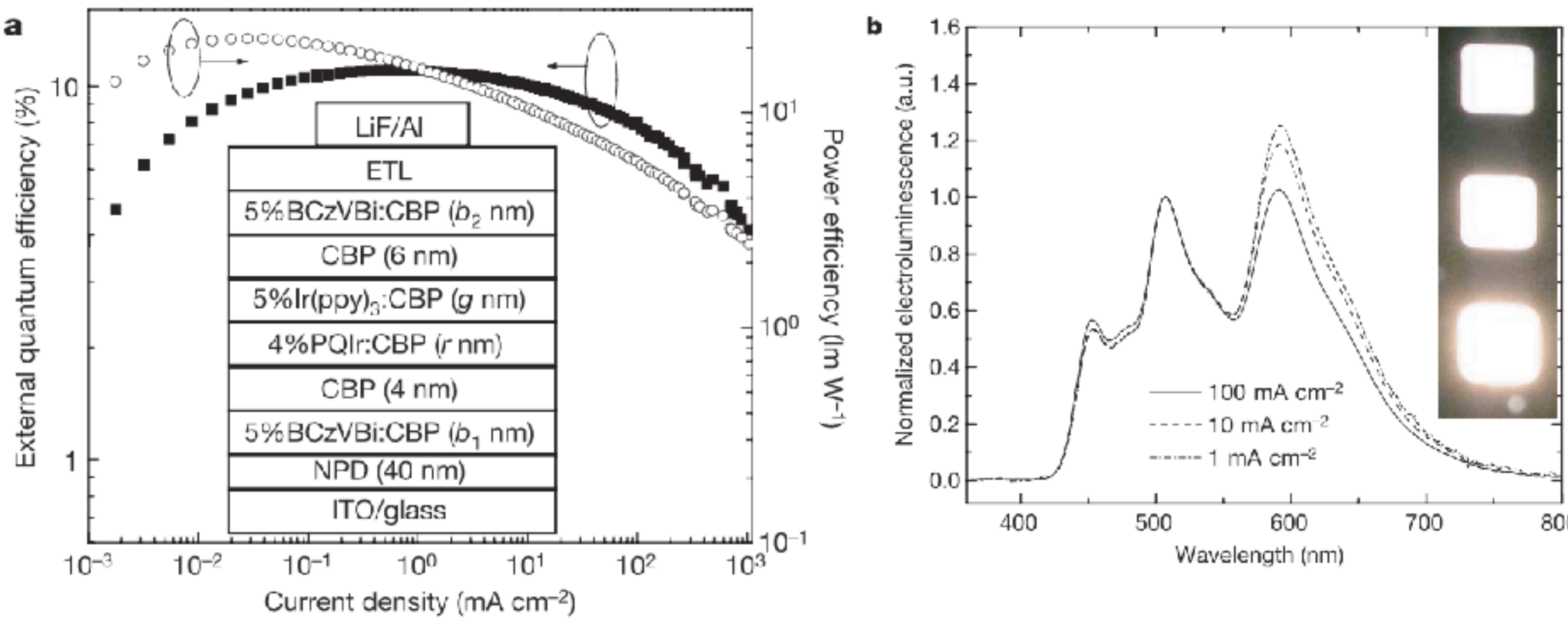
BCzVBi



Ir(ppy)$_3$



PQIr



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White OLEDs (WOLEDs)

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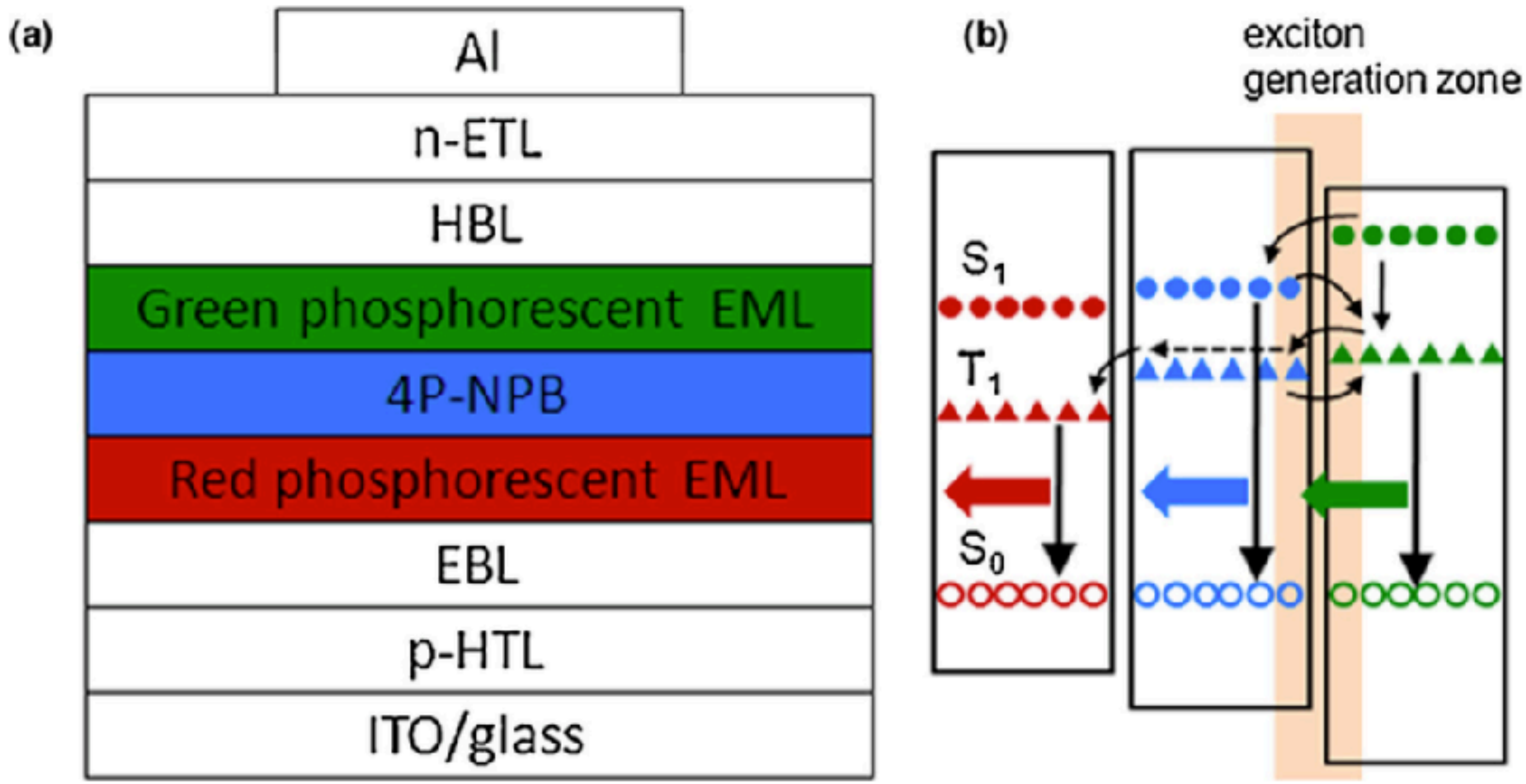
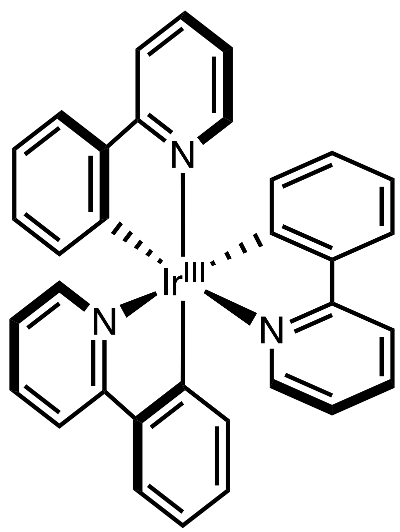
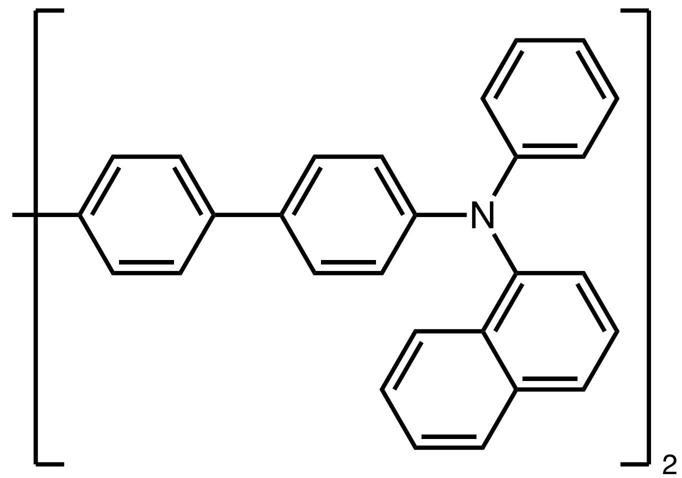


Chen, J.; Zhao, F.; Ma, D. *Mater. Today* **2014**, *17*, 175.
Schwartz, F.; Pfeiffer, M.; Reineke, S.; Walzer, K.; Leo, K. *Adv. Mater.* **2007**, *19*, 3672.

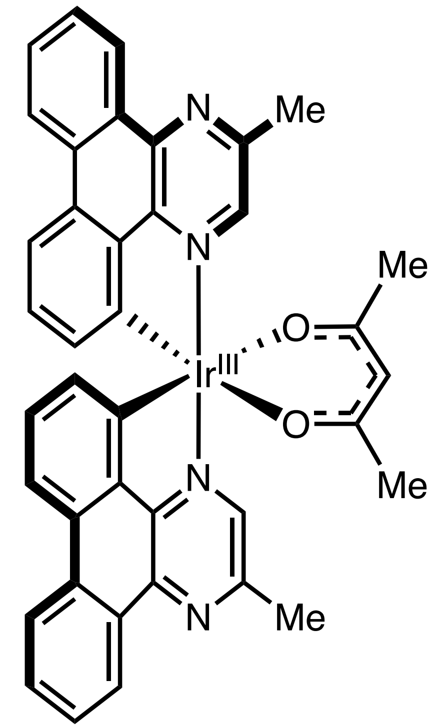
White OLEDs (WOLEDs)



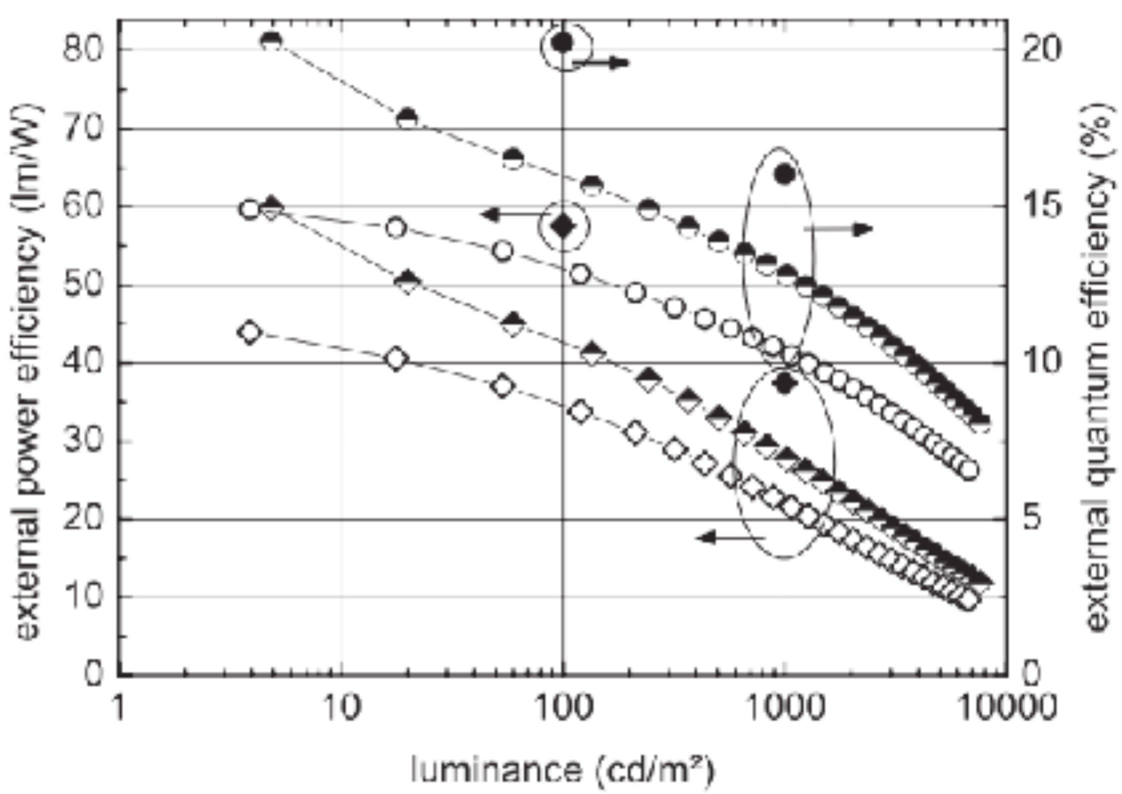
$Ir(ppy)_3$

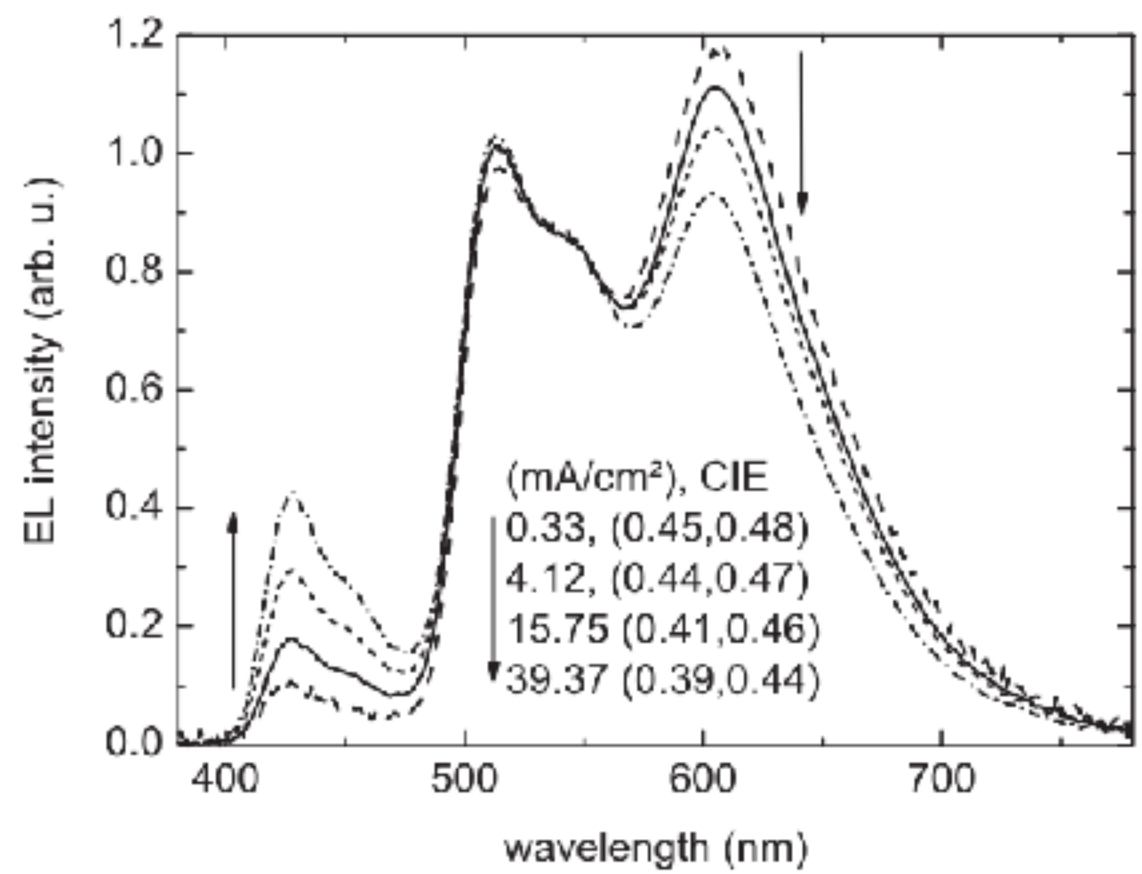


4P-NPD



$Ir(MDQ)_2(acac)$

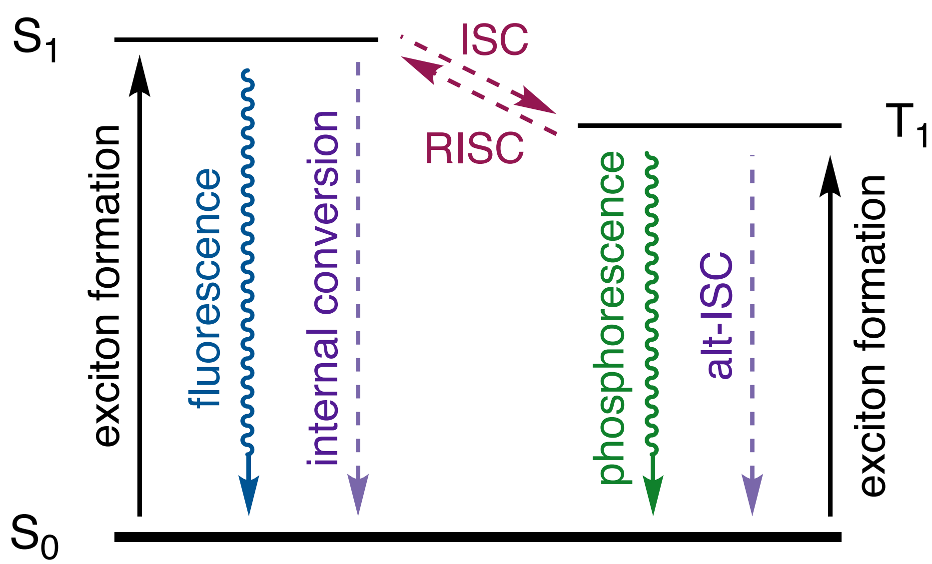


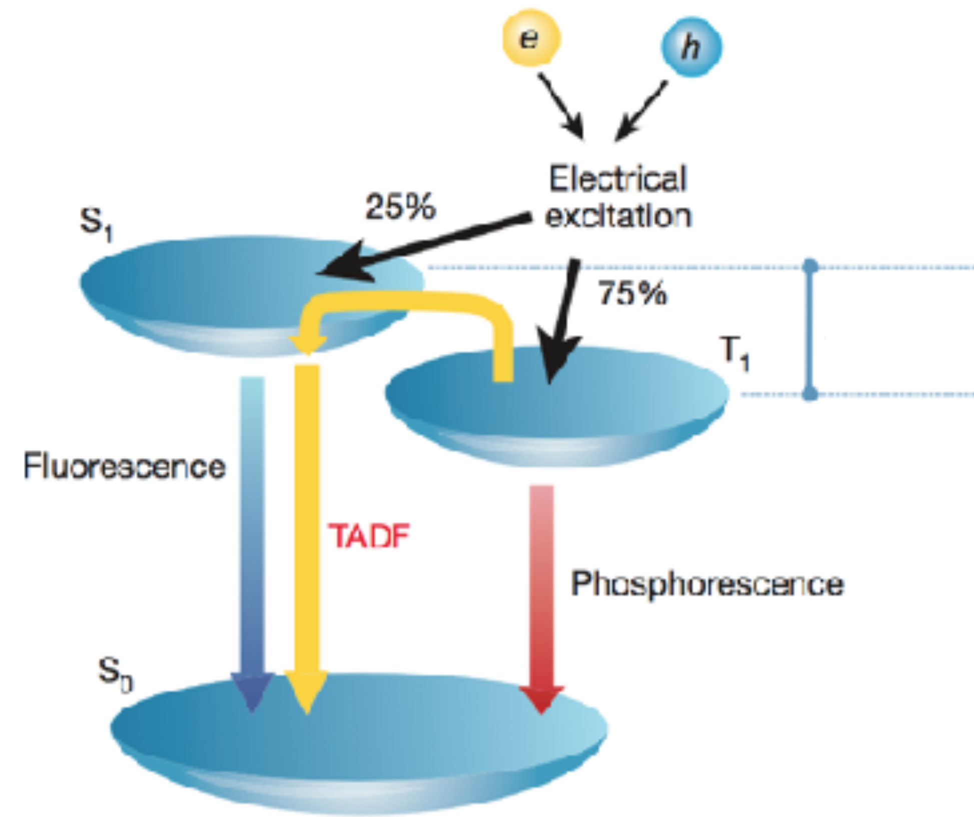


Chen, J.; Zhao, F.; Ma, D. *Mater. Today* **2014**, *17*, 175.
Schwartz, F.; Pfeiffer, M.; Reineke, S.; Walzer, K.; Leo, K. *Adv. Mater.* **2007**, *19*, 3672.

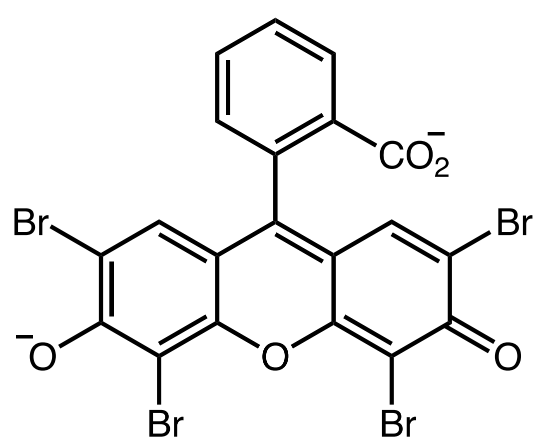
Thermally-Activated Delayed Fluorescence (TADF)

Obviously not phosphorescence





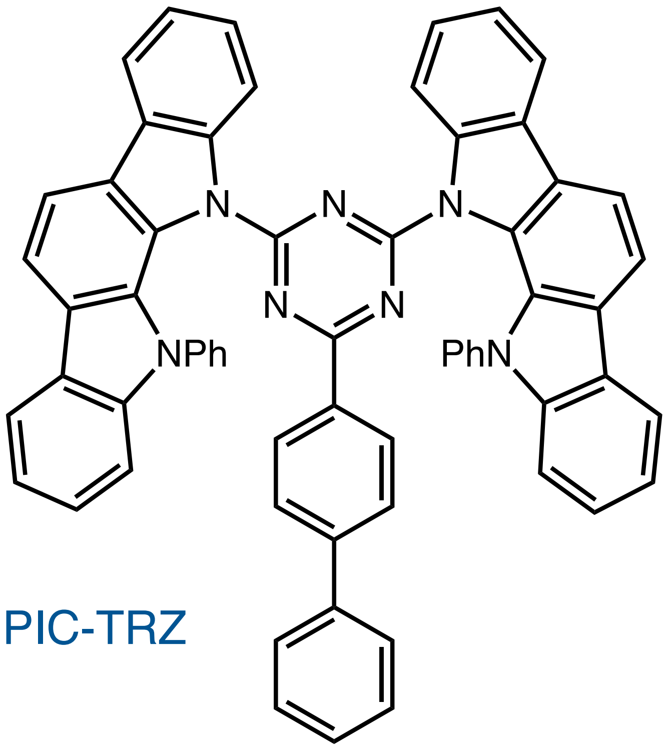
eosin Y, 1961
(E-type delayed fluorescence)



"the high-frequency band (which has a contour identical with the fluorescence band) is the result of thermal activation to the upper singlet level folowed by a radiative transition from there to the ground state, and we shall therefore call this the delayed fluorescence band"

Parker, C. A.; Hatchard, C. G. *Trans. Faraday Soc.* **1961**, *57*, 1894.
Yang, Z. *et al. Chem. Soc. Rev.* **2017**, *46*, 915.

Thermally-Activated Delayed Fluorescence (TADF)



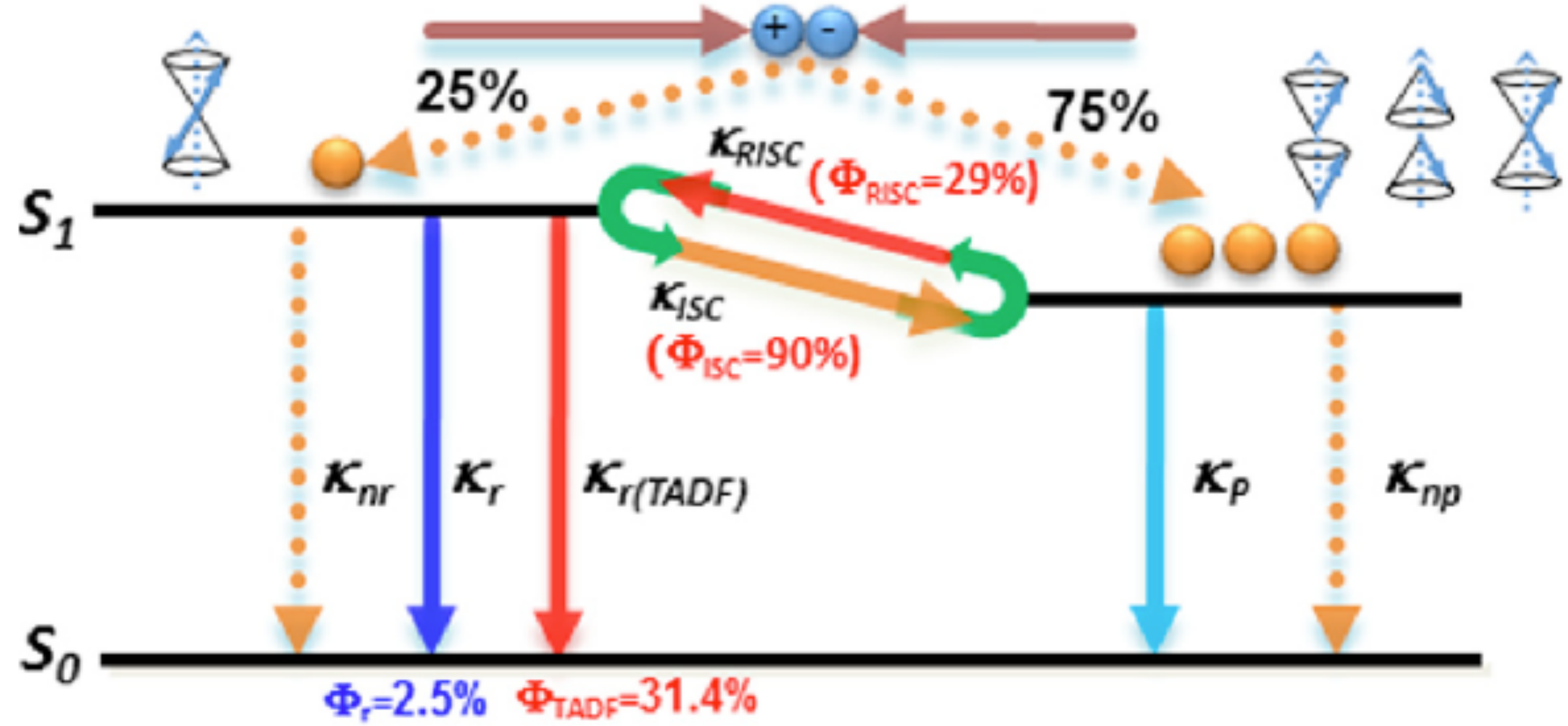
PIC-TRZ

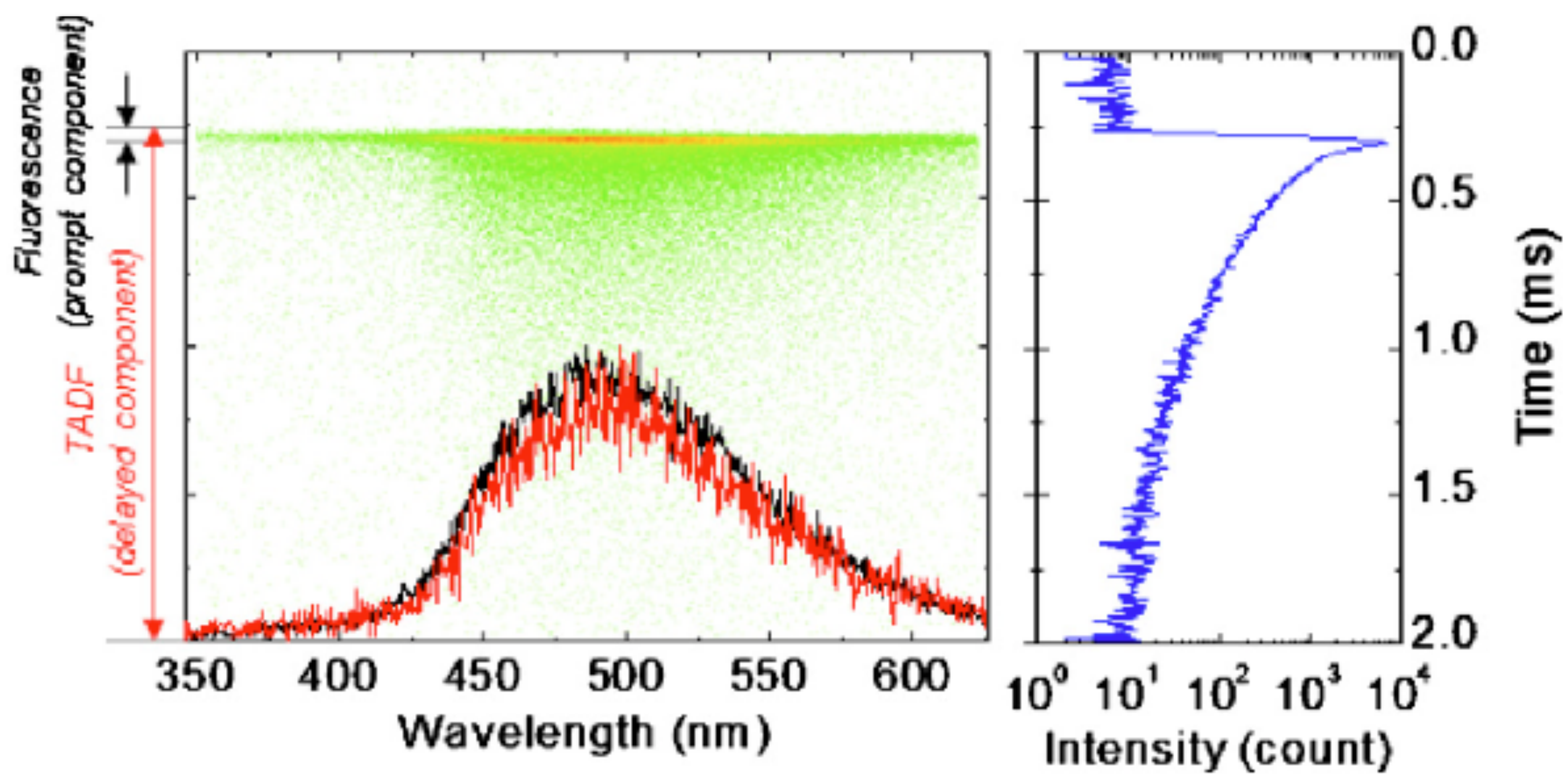
$E(T_1) = 2.55$ eV

$E(S_1) = 2.66$ eV

$\Delta E_{ST} = 0.11$ eV

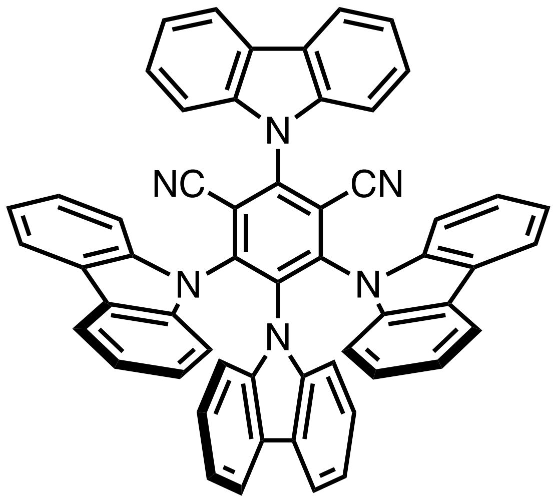
$\eta_{ext} = 5.3\%$



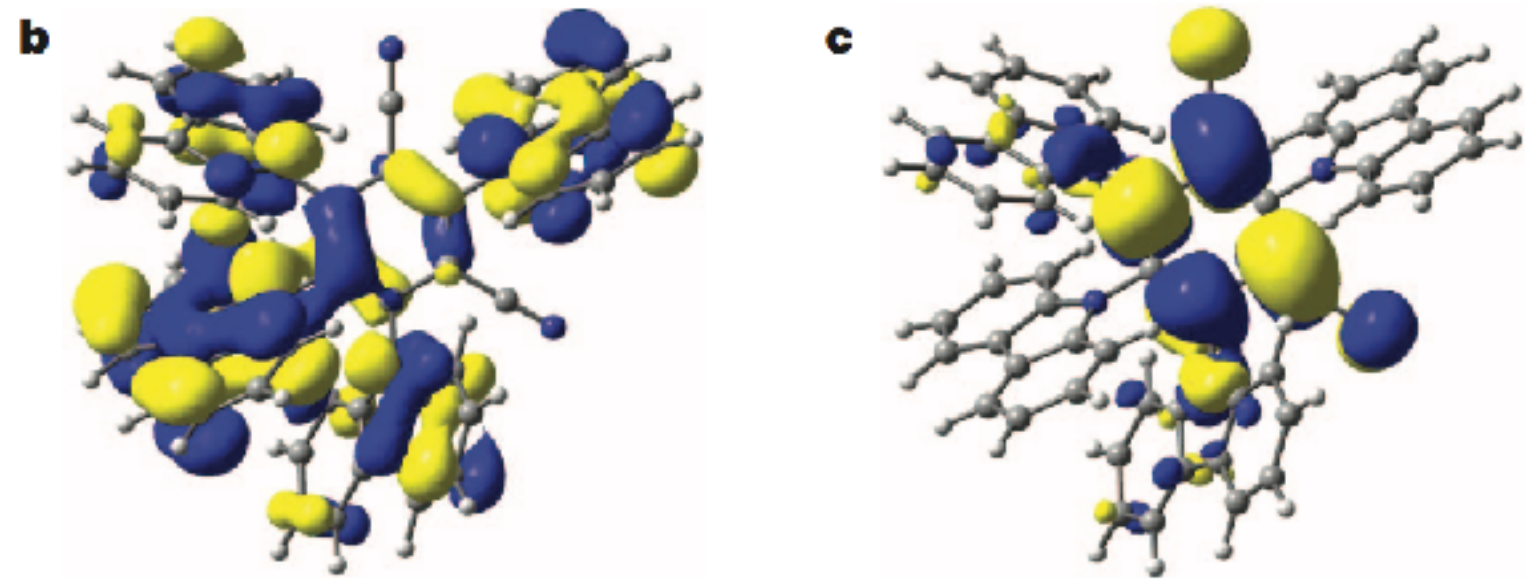


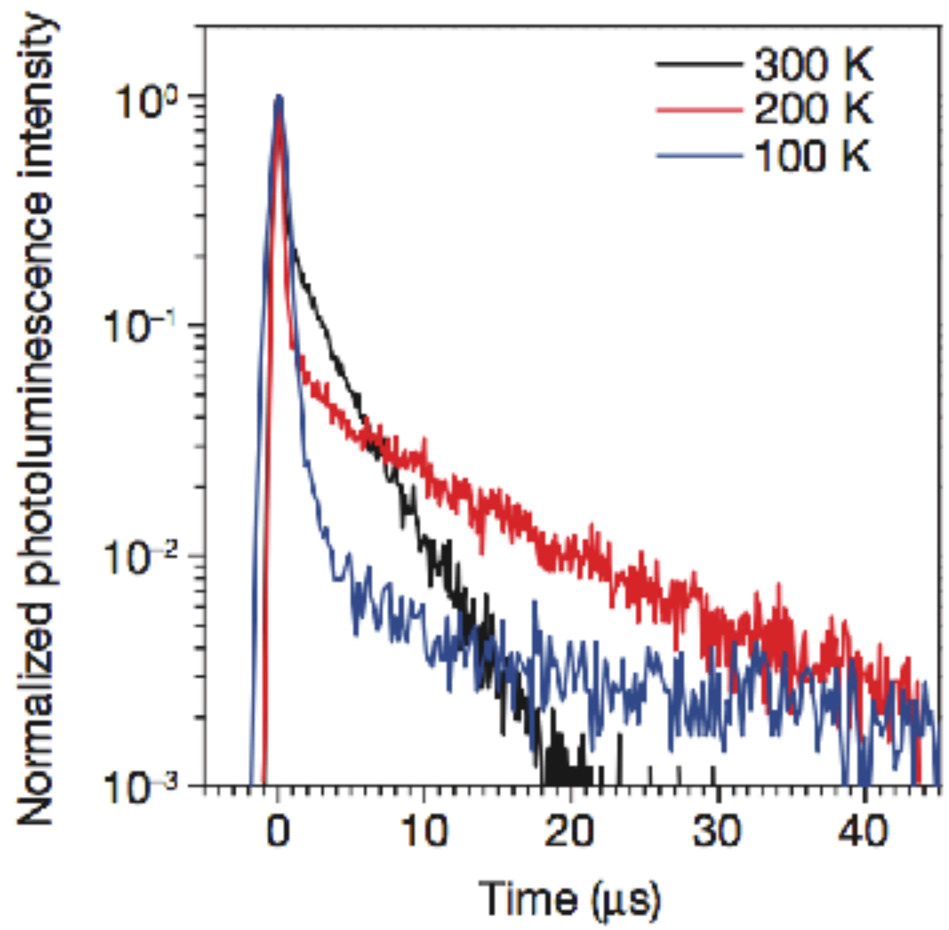
Adachi, C. *et al. Appl. Phys. Lett.* **2011**, *98*, 083302.
Yang, Z. *et al. Chem. Soc. Rev.* **2017**, *46*, 915.

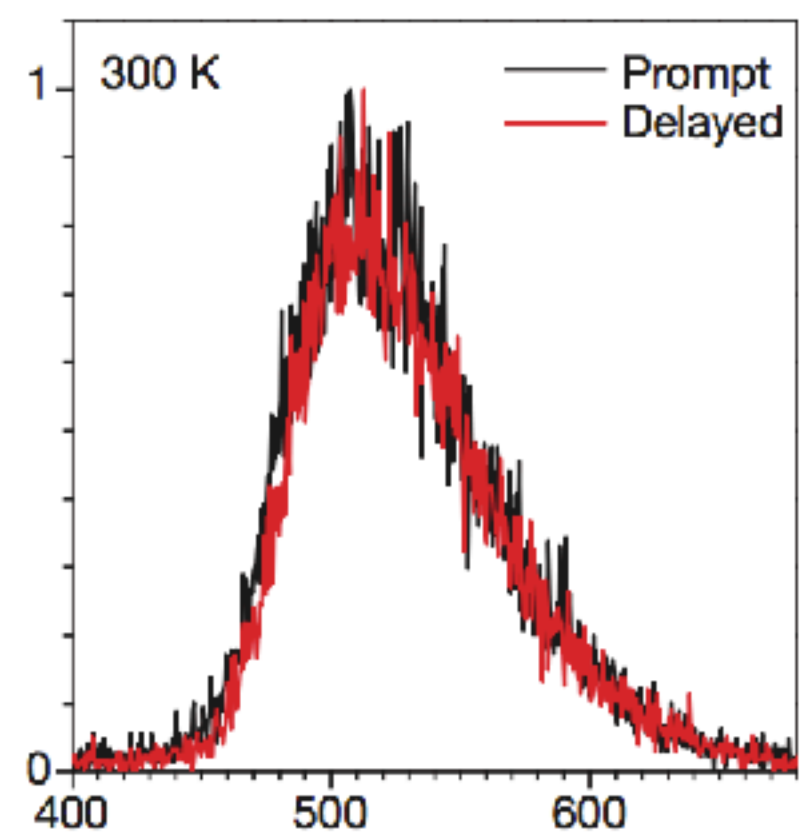
Thermally-Activated Delayed Fluorescence (TADF)



4-CzIPN

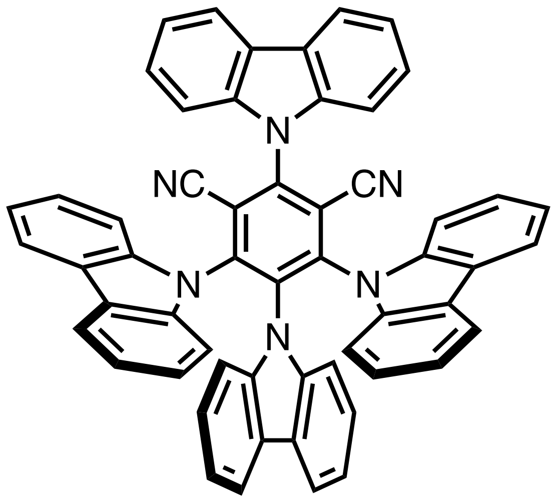




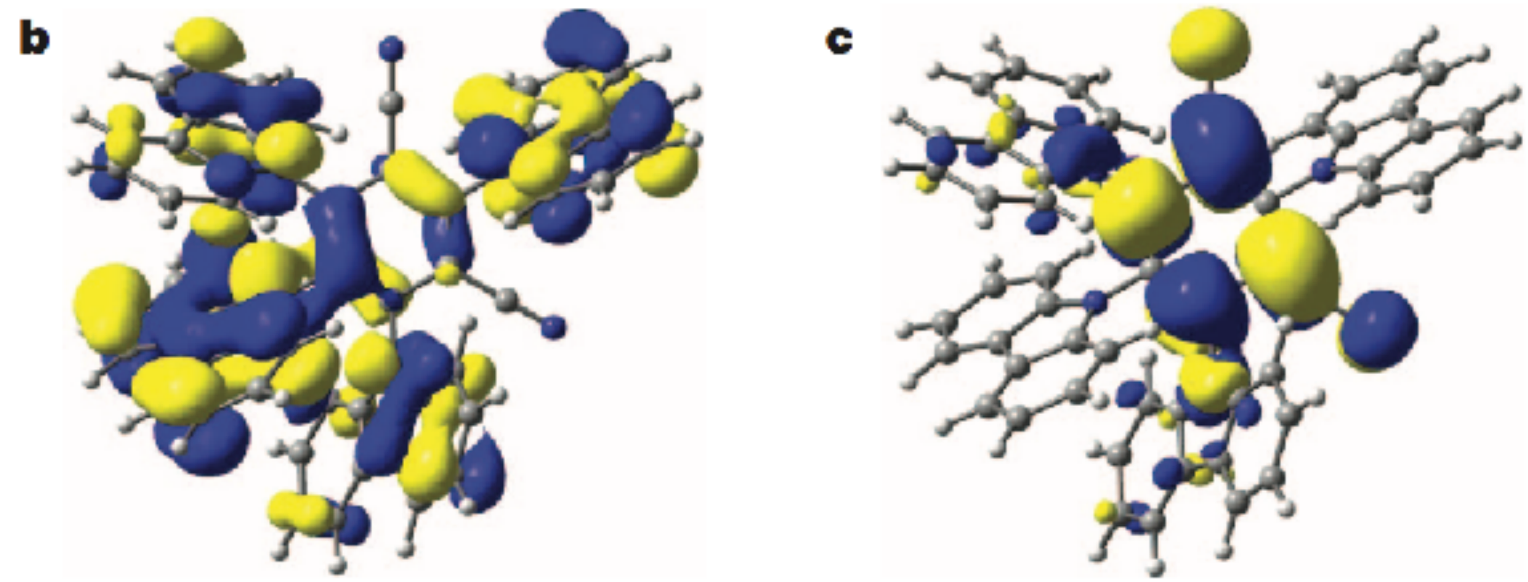


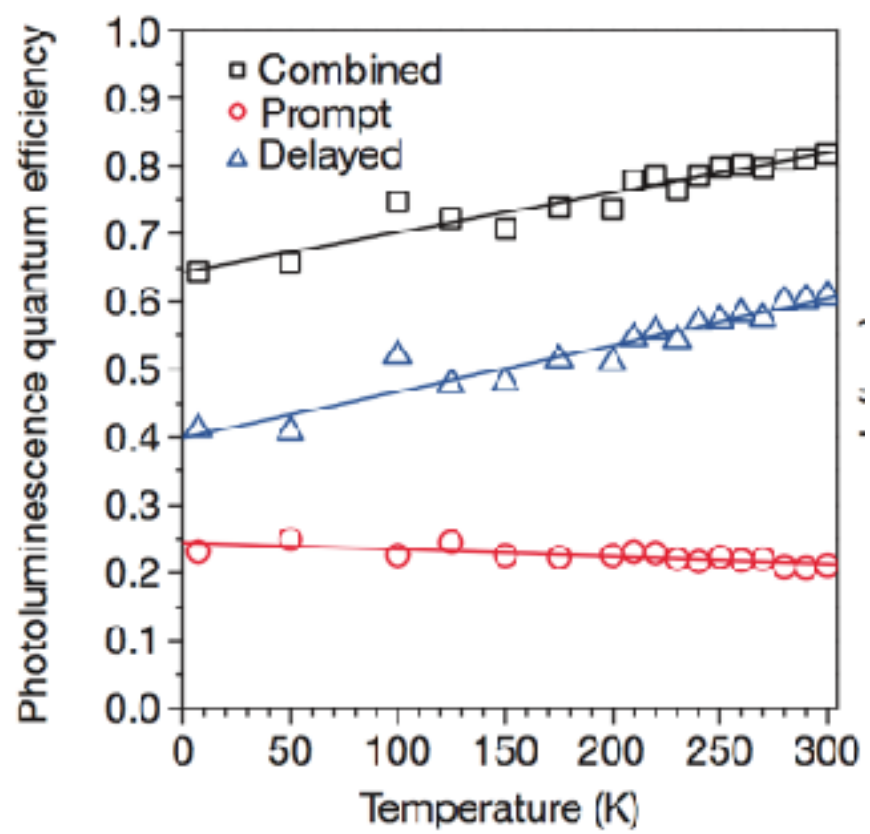
Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. *Nature* **2012**, *492*, 234
Yang, Z. *et al. Chem. Soc. Rev.* **2017**, *46*, 915.

Thermally-Activated Delayed Fluorescence (TADF)



4-CzIPN





Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. *Nature* **2012**, *492*, 234
Yang, Z. *et al. Chem. Soc. Rev.* **2017**, *46*, 915.

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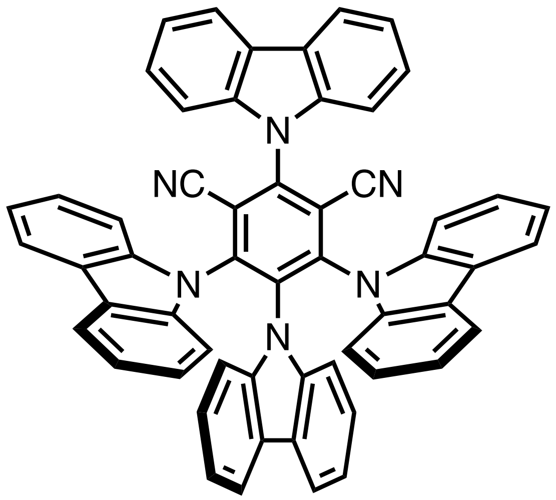
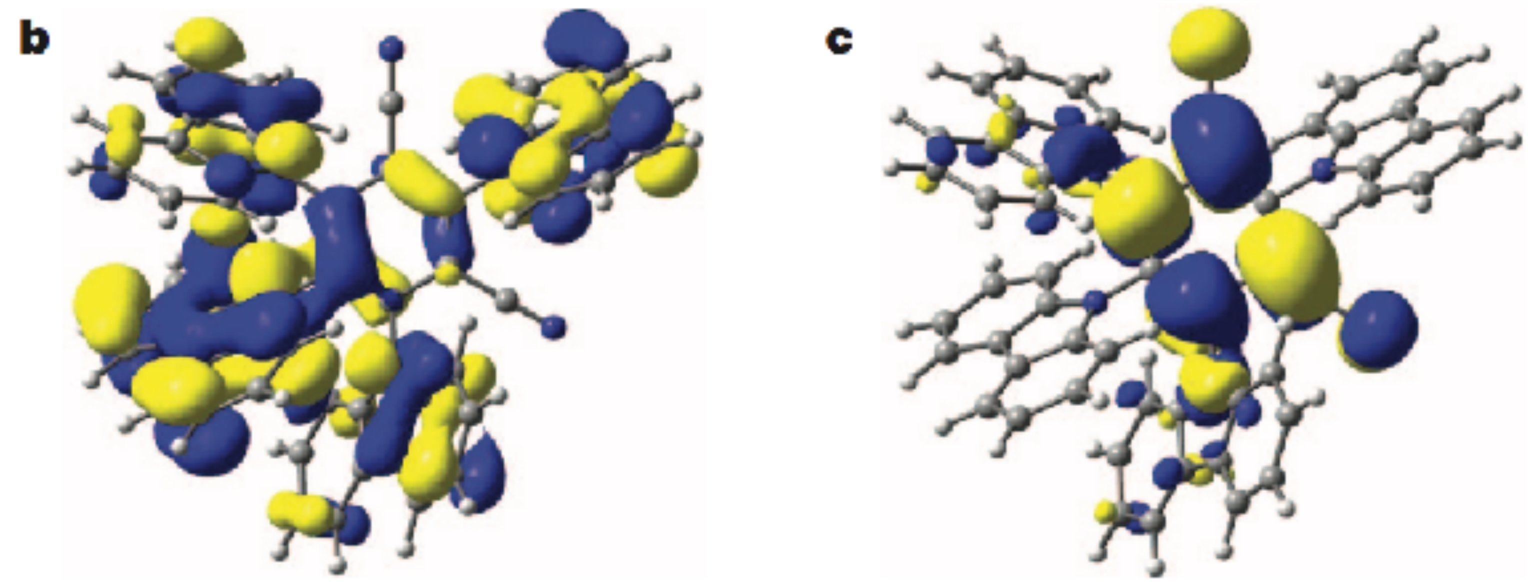
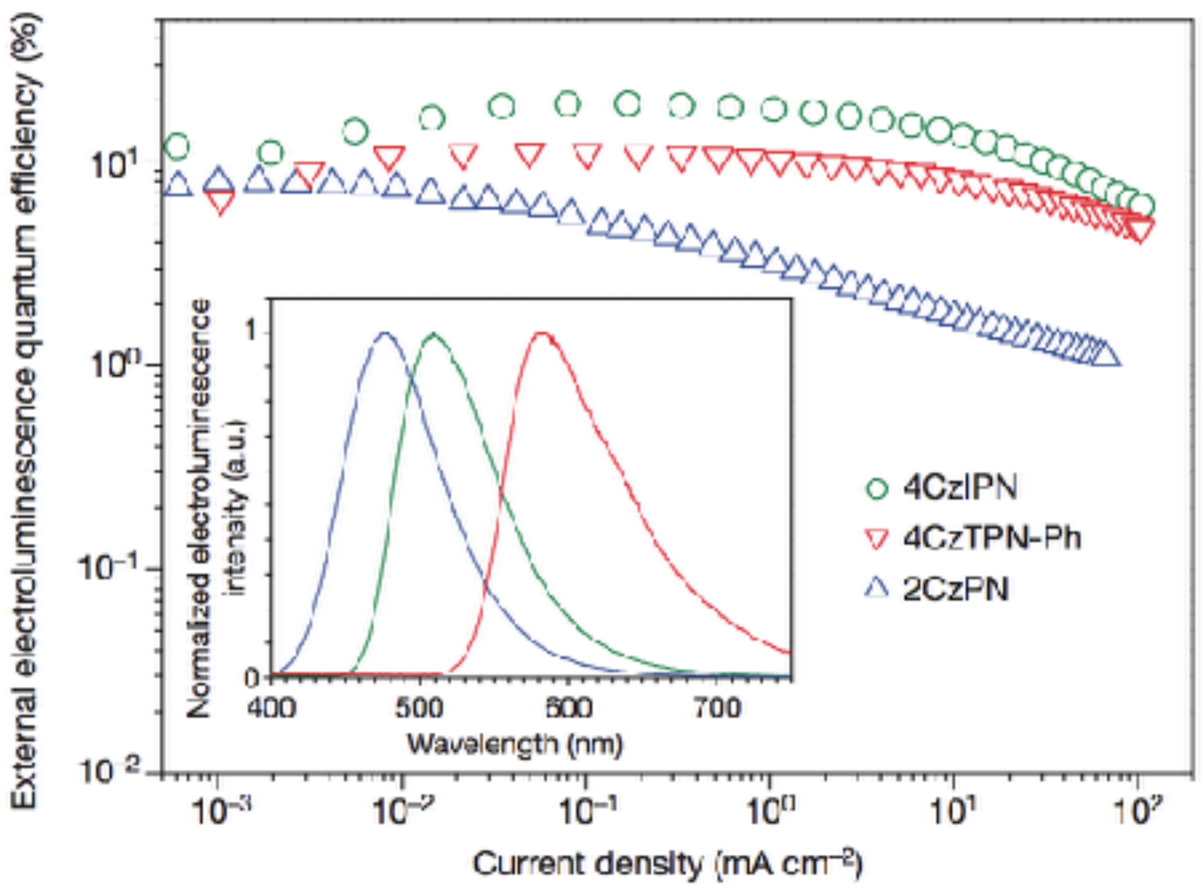


4-CzIPN





η_{ext} = (19.3±1.5)%

"Third-generation organic electroluminescence materials"

335 references in Review below, published Jan 2017

Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. *Nature* **2012**, *492*, 234
Yang, Z. *et al. Chem. Soc. Rev.* **2017**, *46*, 915.