Electrophosphorescence for Solid-State Lighting

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High Efficiency OLED Options

- Multiple emitters for RGB ⇒ white
- **ALL** excitons need to be utilized
- Ir-based emitters: well proven in mobile displays and television
- Thermally Assisted Delayed Fluorescence (TADF)

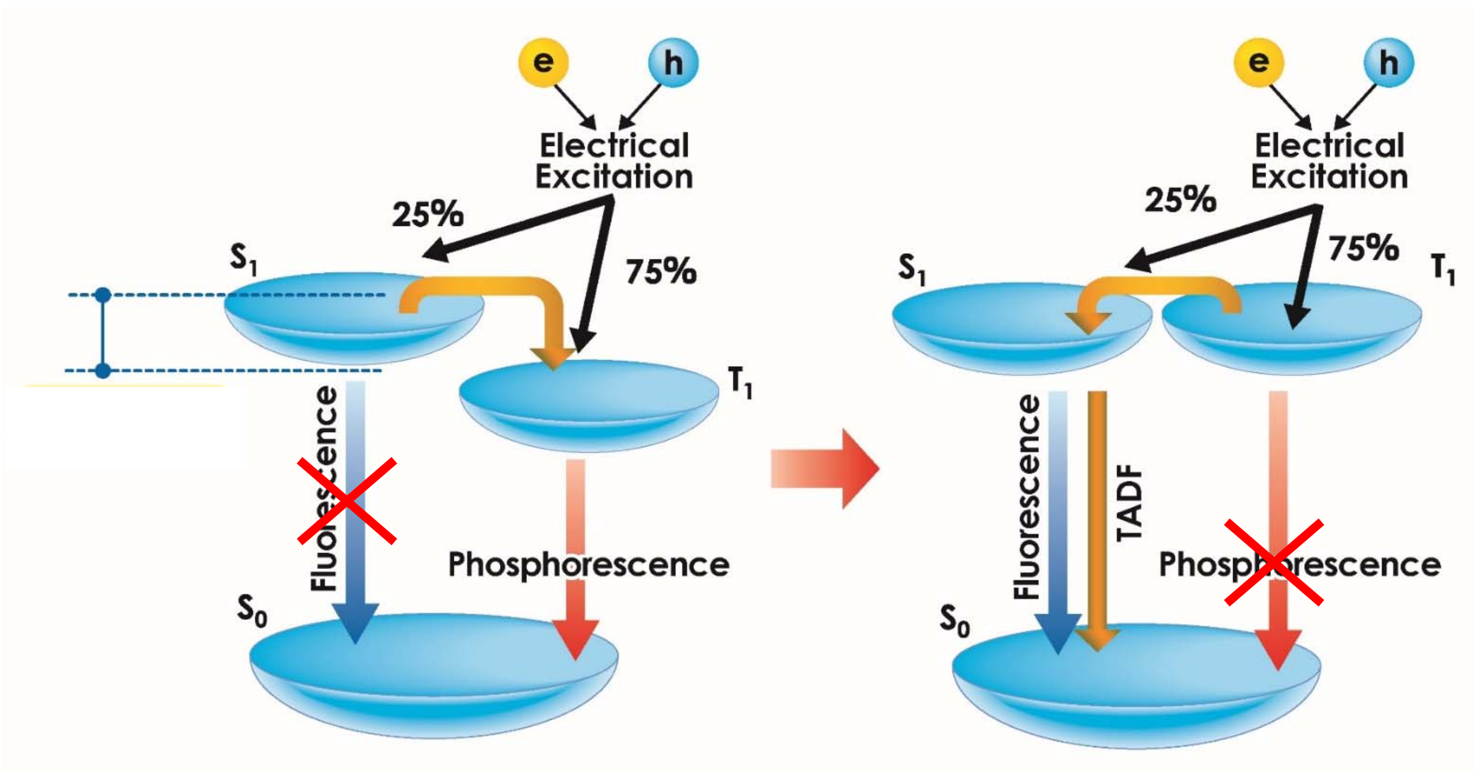
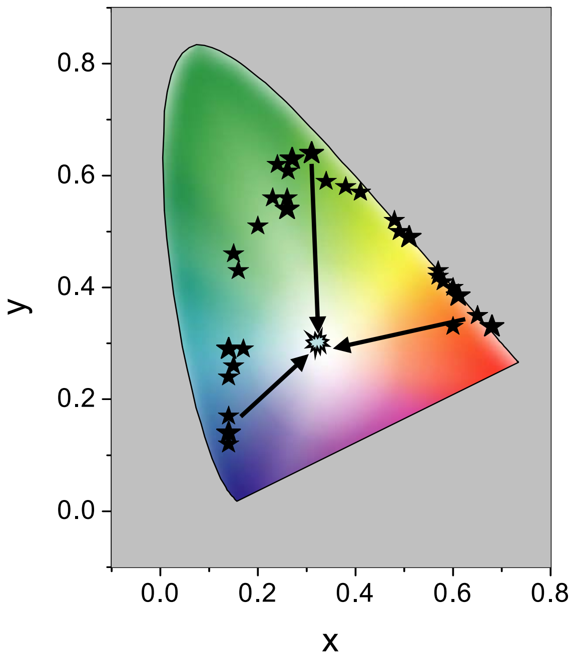
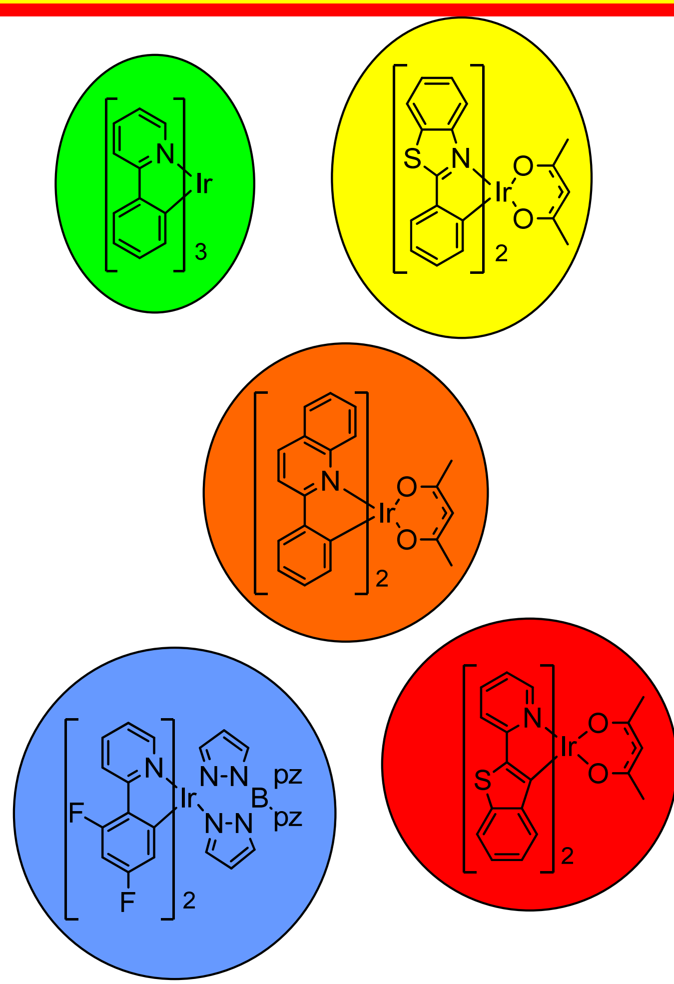


Image from Chihaya Adachi, Kyushi Univ.

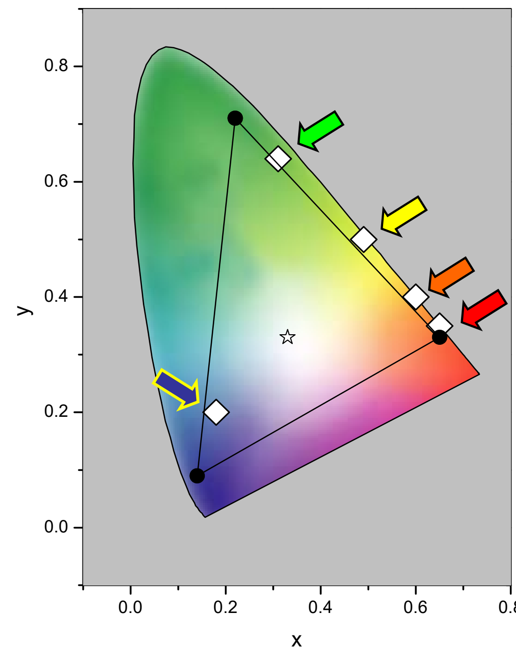
Φ_{int}∼ **100%! Nature, 492, 234 (2012)**

Organometallic Ir complexes in OLEDs





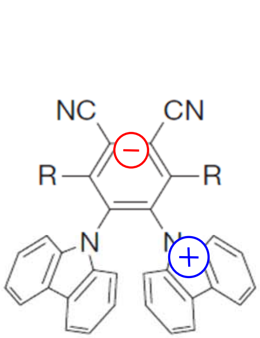
Phosphorescence
efficiency of
Ir emitters
is ~100%



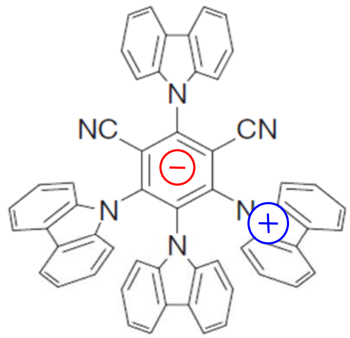
- Efficient phosphorescence with τ = 1-3 μs lifetime
- Optimized OLEDs give external efficiency $\Rightarrow$ Internal efficiency up to 70-100%
- Green, Yellow, Red lifetime are very long, blue is a problem

USC

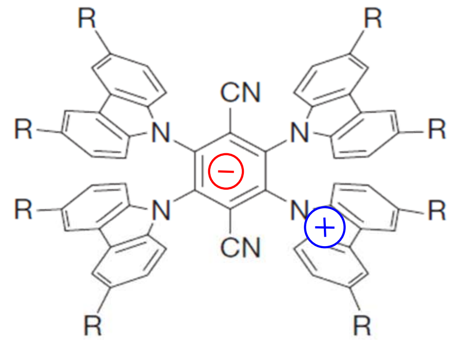
High Efficiency TADF



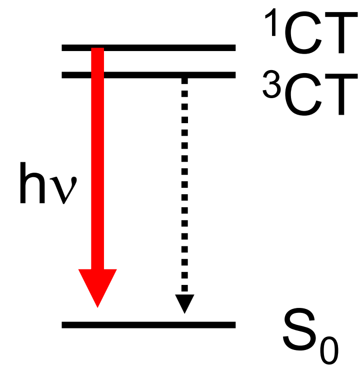
4CzPN: R = carbazolyl
2CzPN: R = H

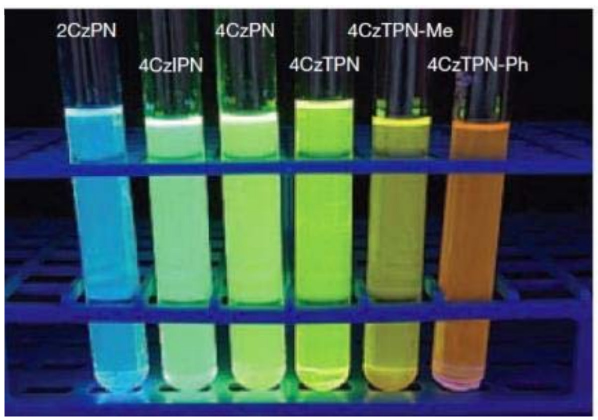


4CzIPN



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





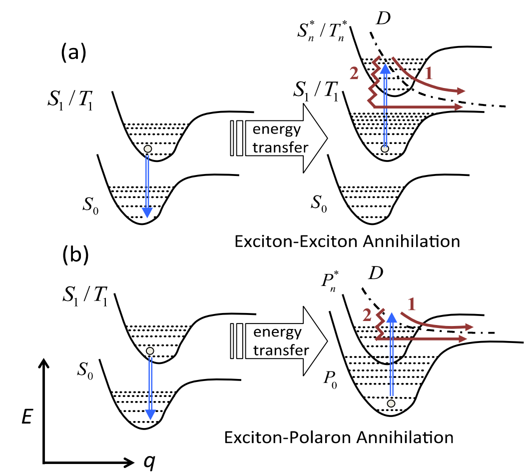
$$k_r(CT^{SOC}) \propto \frac{\langle {}^3CT | H_{SO} | {}^1CT \rangle}{\Delta E_{ST}} \cdot \langle S_0 | er | {}^1CT \rangle$$

- Color (EQE): Green (**19.3%**), Orange (11.2%), Sky Blue (8%)
  - Uoyama, *et. al.*, *NATURE*, **2012**, *492*
- Orthogonal donor-acceptor give CT excited state with small ΔE_{ST}
- τ ~ 5 μs or higher, no metal to enhance SOC, weak ^1CT oscillator

Phosphors and TADF Emitters good, what's the problem?

- What about device lifetime?
  - **Green** and **Red** >30 years at display intensity ☺
  - **Blue** <2 years at display brightness ☹

- Device degradation is due to **bimolecular annihilation***
  - (a) TTA: $T_1 + T_1 \rightarrow S_0 + S_n$(hot)
  - (b) TPA: $T_1 + H^- \rightarrow S_0 + H^-$(hot)
  - **G**/**R**: S_n(hot) or H^-(hot) $\Rightarrow$ relax to GS
  - **B**: S_n(hot) or H^-(hot) $\Rightarrow$ degradation

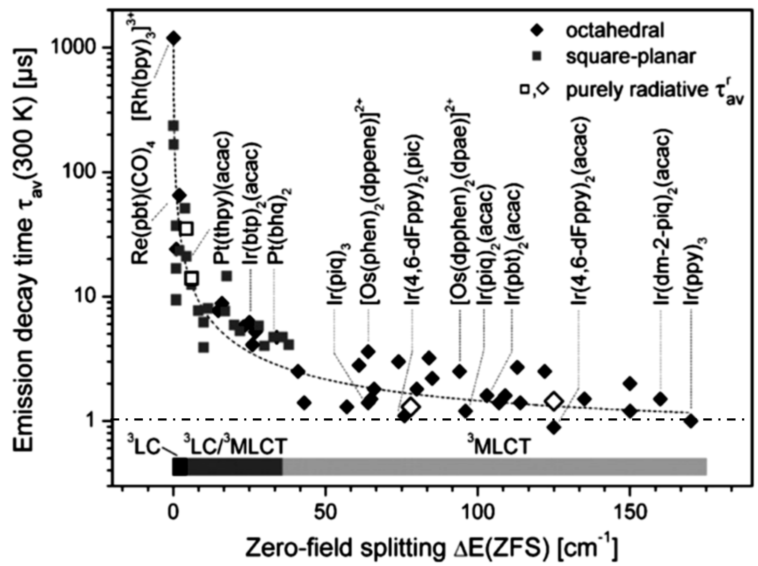


- OLED displays: Ir-based emitters for **Green**
  organic fluorescent dopant for **Blue**
  - nsec lifetime of **Blue** fluorescence decreases bimolecular decay

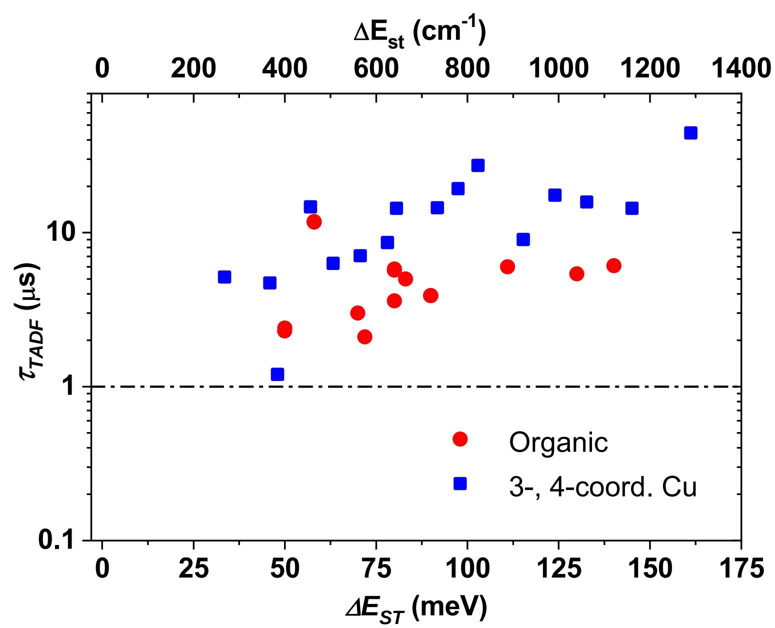
* N. Giebink, *et al., J. Appl. Phys.* **2008,** *103*, 044509

Best phosphor and TADF Lifetimes ~ 1 μs

- Ir and Pt based phosphors seem to flat- line at ~ 1 μs (H. Yersin, *et al.*, *Coord. Chem. Rev.* **2011**)



- TADF based emitters hit 1-2 μs baseline, most are in neat solids not doped films (Organic: Liu, Y., *et al. Nature Rev. Mat.*, **2018**) (Copper: R. Czerwieniec, *et al.*, *Coord. Chem. Rev.* **2016**)

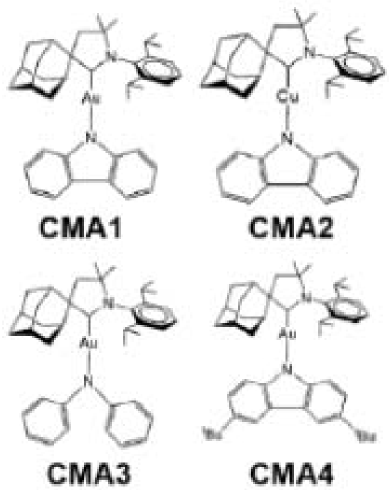


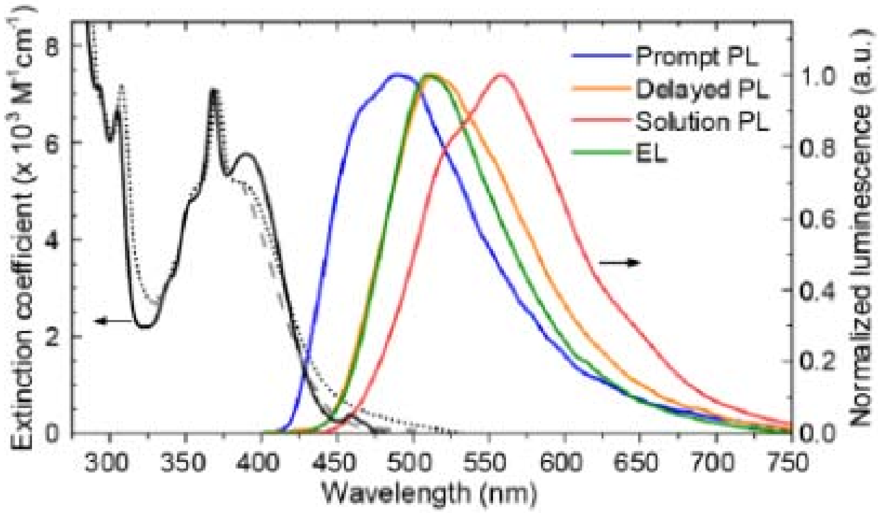
2-coordinate CAAC-M-Cz

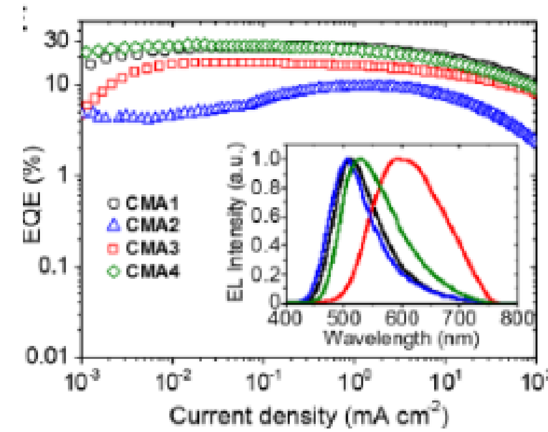
Science REPORTS

Cite as: D. Di *et al.*, *Science* 10.1126/science.aah4345 (2017).

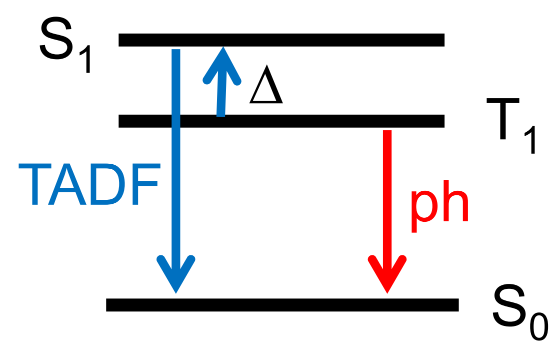
High-performance light-emitting diodes based on carbene-metal-amides





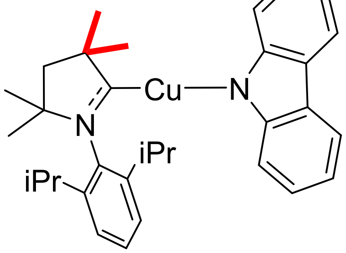


- Clearly both singlet and triplet are utilized
- Are these “normal” phosphors or TADF?
- Very little photophysical characterization



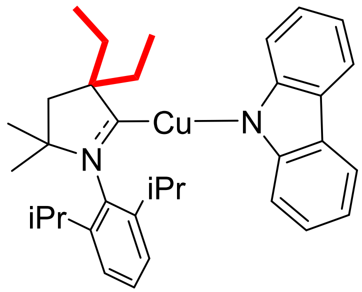
D. Dai, D. Credgington, R. Friend, M. Bochmann, *et al., Science*, **2017**

CAAC-Cu-Cz complexes



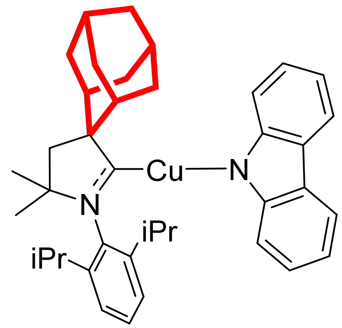
Me$_2$

Φ_{PL} = 11%



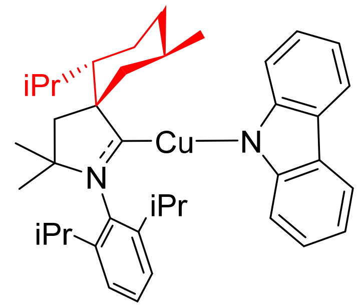
Et$_2$

Φ_{PL} = 56%



Ad

Φ_{PL} = 68%



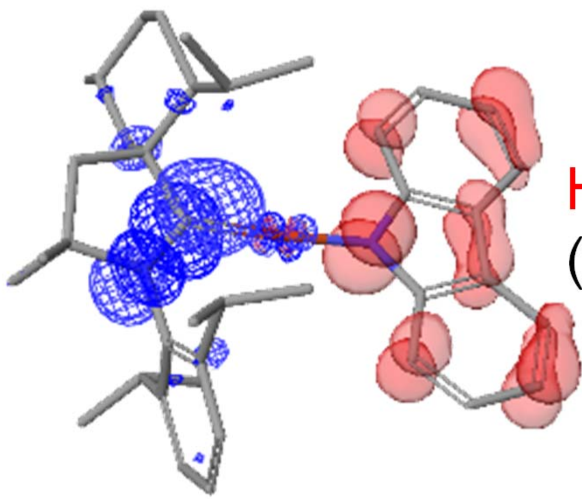
Men

Φ_{PL} = 100%

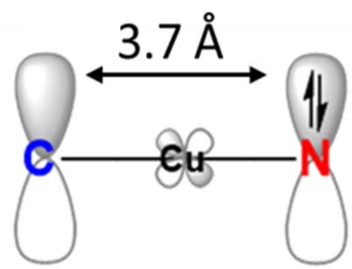
in solution and doped thin film

Increasing Φ_{PL} **IN SOLUTION**

LUMO (mesh)



HOMO (solid)

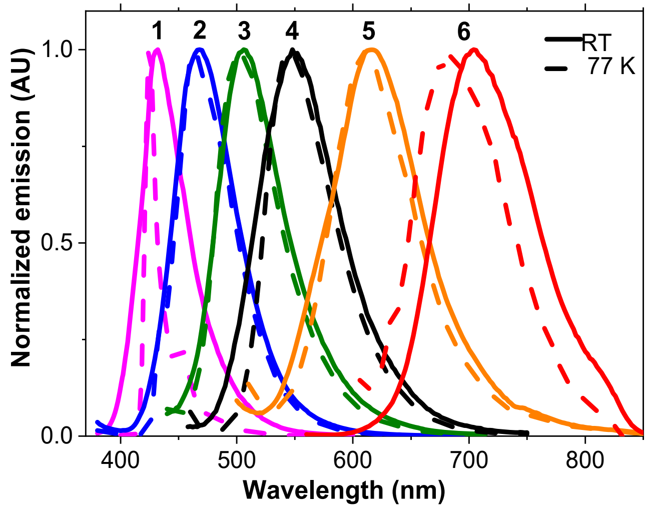


Excited state is interligand charge transfer (ICT), NOT MLCT

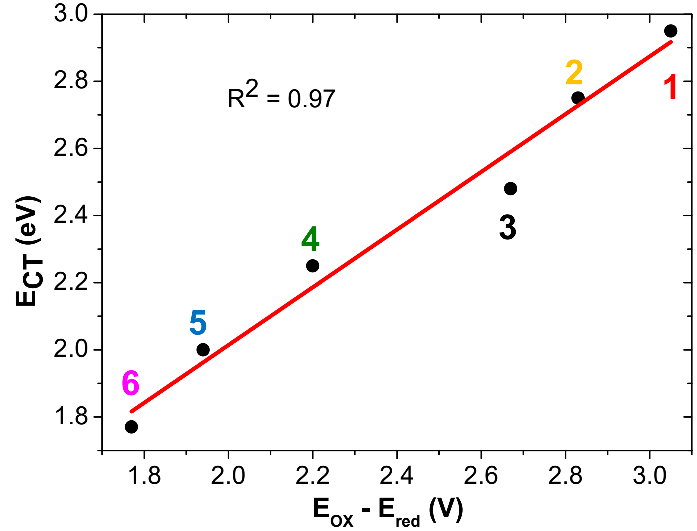
R. Hamze, *et al.*, *Science*, **2019**

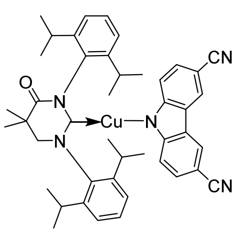
Absorption (THF) and emission (PS thin film) spectra

1% doped polystyrene thin film

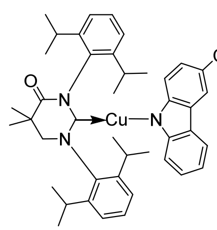


THF Solution

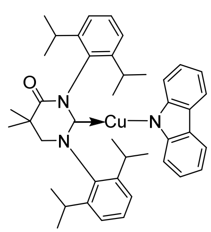




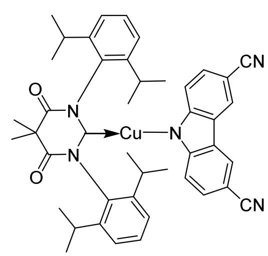
MAC*CuCzCN2 (1)



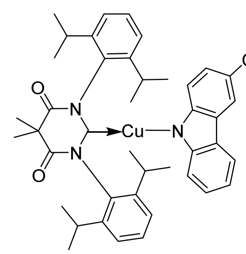
MAC*CuCzCN (2)



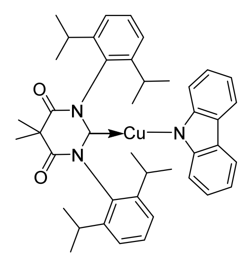
MAC*CuCz (3)



DAC*CuCzCN2 (4)



DAC*CuCzCN (5)



DAC*CuCz (6)

^{3}Cz + ^{1,3}CT
Φ_{PL}(RT)= 80%

Φ_{PL} (RT)= 80-100%
τ = 1-1.5 μs
(k_r = 7 x 10^5 s^{-1})

Energy gap law problem
Φ_{PL} (RT)= 30, 2%

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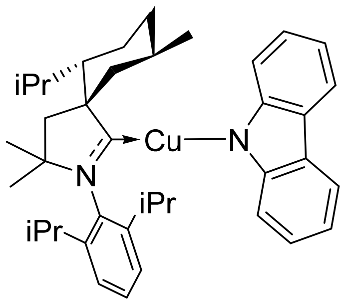
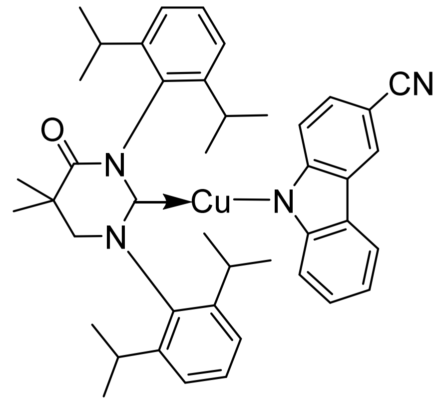
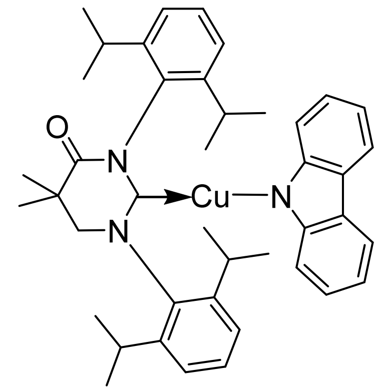
S. Shi, *et al.*, *JACS*, **2019**

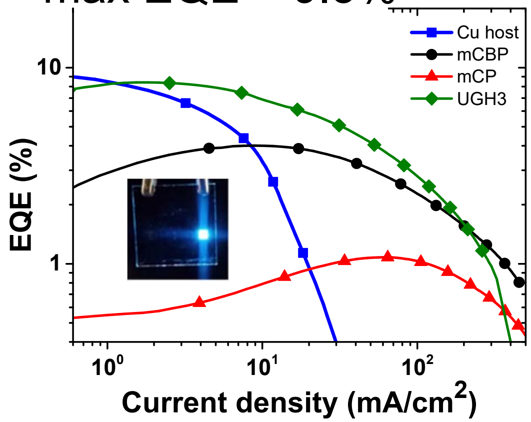
(carbene)Cu(Cz) based OLEDs



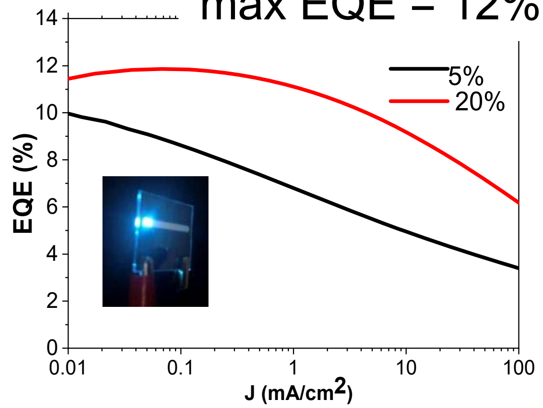




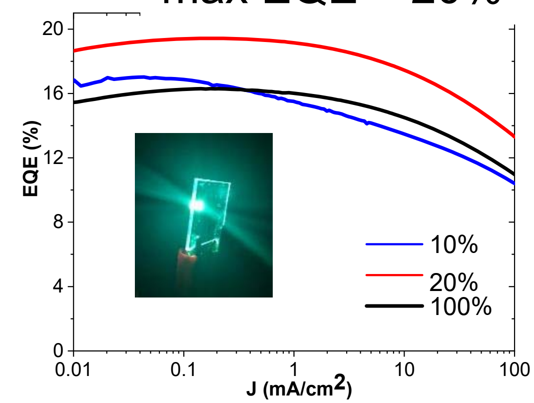
max EQE = 9.5%



max EQE = 12%



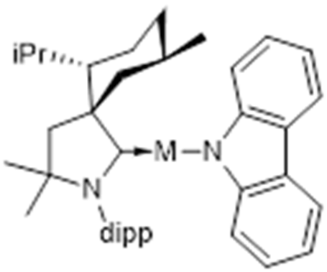
max EQE = 20%

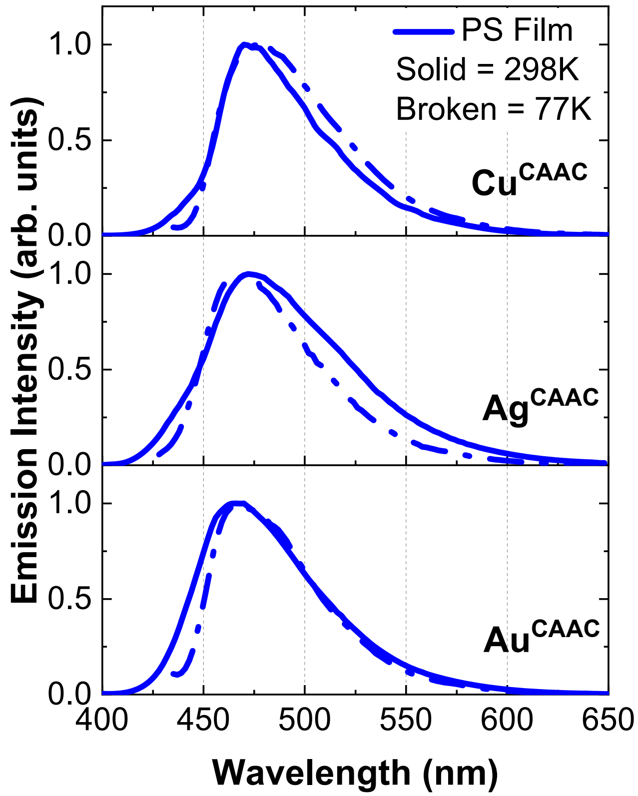


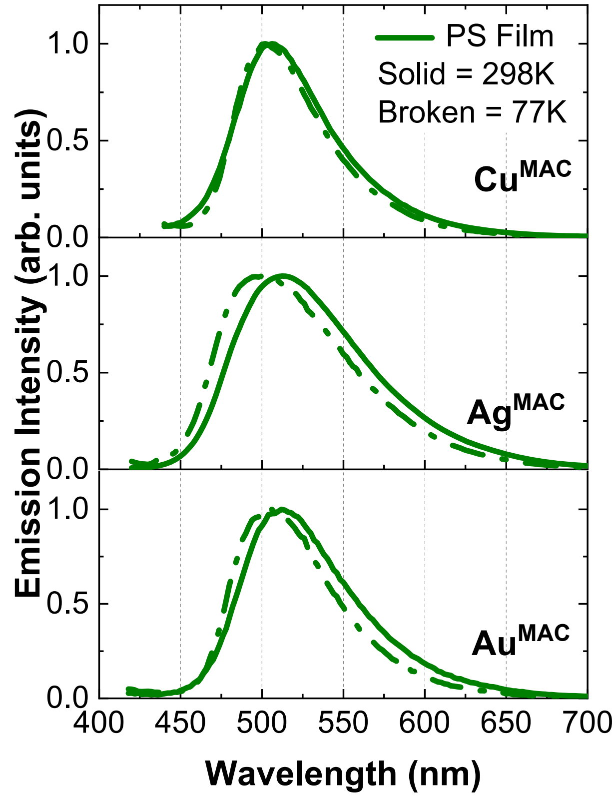
R. Hamze, *et al.*, *Science,* **2019**

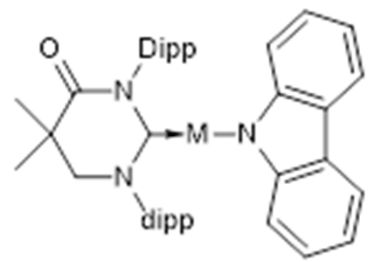
S. Shi, *et al.*, *JACS,* **2019**

Copper, Silver, Gold Based Phosphors









Blue Emission

	Φ_{PL}	τ (μs)
Cu	1.0	2.8
Ag	1.0	0.5
Au	1.0	1.1

Green Emission

	Φ_{PL}	τ (μs)
Cu	0.9	1.4
Ag	0.8	0.33
Au	0.9	0.83

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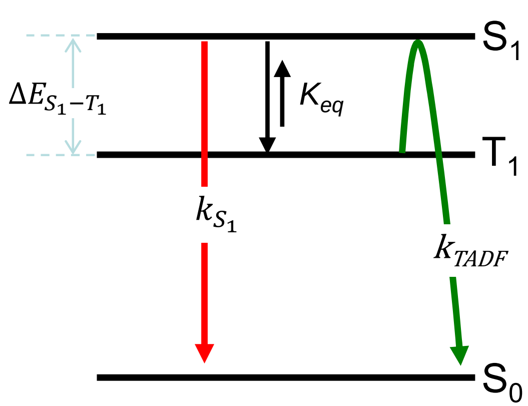
R. Hamze, *et al.*, *JACS*, **2019**

Where is the best place to look for lower τ_{TADF}?

- Intersystem crossing here is very fast, τ (ISC) = 20-200 ps
- Ag shows the fastest TADF rate primarily due to small $\Delta E_{S_1-T_1}$
- In the limit of very fast ISC: $\tau_{TADF} = {}^{\tau_{S_1}}/_{K_{eq}}$; † $K_{eq} \propto \exp(\Delta E_{S_1-T_1})$ *

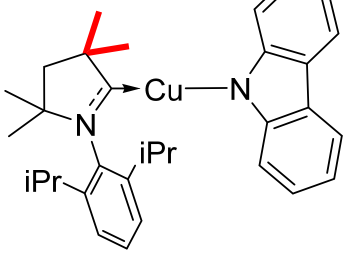


	τ_{meas}	τ_{rad}	**Full kinetic scheme** 200-325K	
	(µs)	(µs)	$\Delta E_{S_1-T_1}$ (cm^{-1})	τ_{S_1} (ns)
Cu^{CAAC}	2.8	2.8	590	73
Ag^{CAAC}	0.50	0.50	150	85
Au^{CAAC}	1.1	1.1	570	25
Cu^{MAC}	1.4	1.6	570	28
Ag^{MAC}	0.33	0.42	180	46
Au^{MAC}	0.83	0.98	570	24

- Is decreasing $\Delta E_{S_1-T_1}$ further useful?
  - Consider K_{eq} at 300K for Ag^{CAAC}
  - ΔE_{ST} = 150 cm^{-1} ⇒ K_{eq} = 0.16
  - ΔE_{ST} = 50 cm^{-1} ⇒ K_{eq} = 0.26
    τ_{TADF} = 330 ns
  - Decreasing τ_{TADF} further will require a decrease in τ_{S_1}

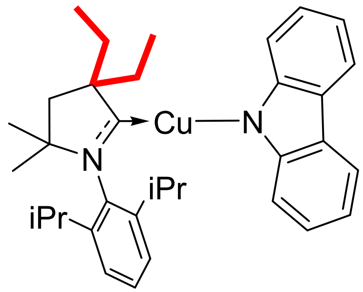
† D. Sylvinson M.R., M.E. Thompson, *et al.*, *Mat. Horiz.*, **2020**
* P. F. Jones, A. R. Calloway, *Chem. Phys. Lett.*, **1971**

What makes (carbene)Cu-Cz complexes work?



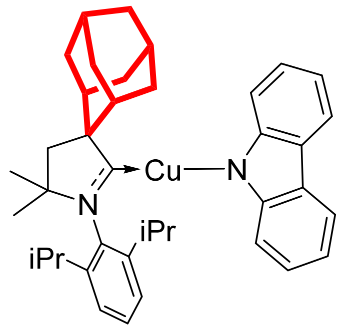
Me_2

Φ_{PL} = 11%



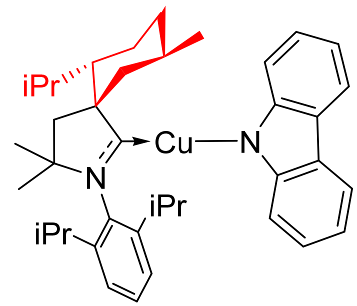
Et_2

Φ_{PL} = 56%



Ad

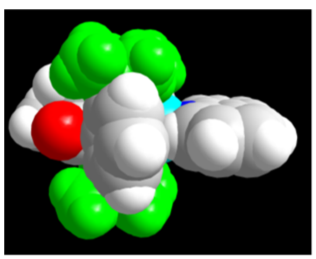
Φ_{PL} = 68%

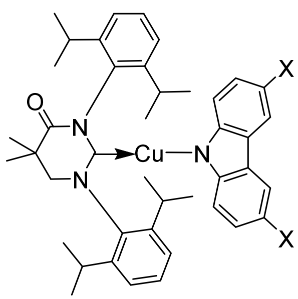


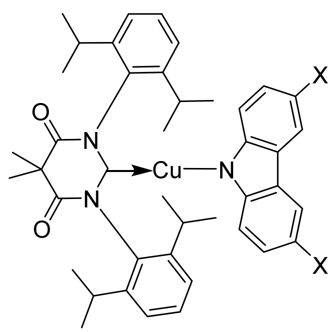
Men

Φ_{PL} = 100%

in solution and doped thin film







High efficiency for violet→orange emitters
Low efficiency if Dipp replaced with phenyl

Are sterically bulky ligands required? What do they do?

- Keep C:→M-N linear
- Prevent rotation about the C-M or M-N bonds
- Prevent the formation of exciplexes and ligand rotation

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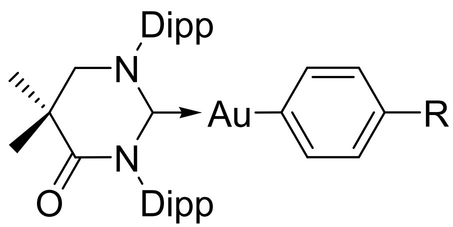
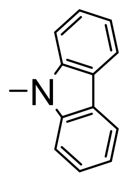
Origin of high efficiency for two-coordinate complexes

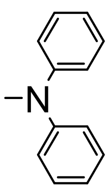


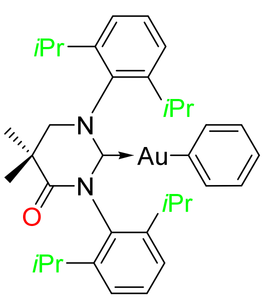
MLCT
exctied
state
(C$^-$-Au$^+$-N)

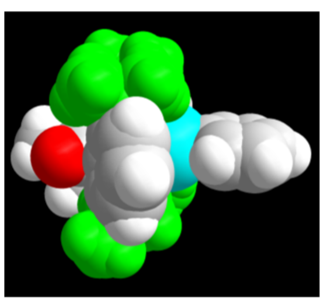
H: R=H

Cz: R= −N 

ICT
exctied
state
(C$^-$-Au-N$^+$)

Nϕ_2: R= −N 

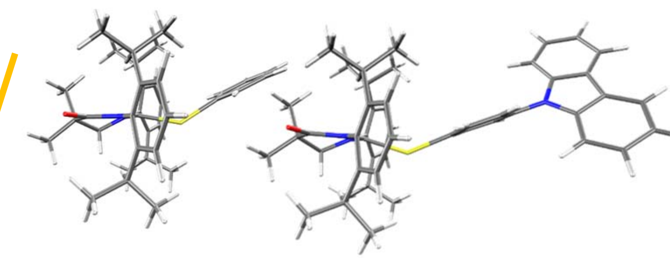




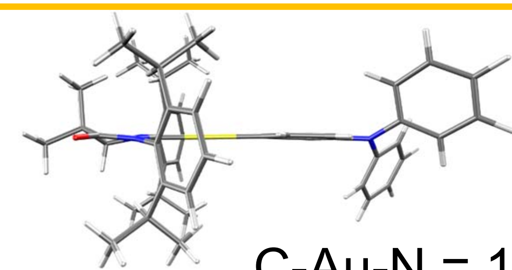
No steric constraints on ligand rotation

Complex	PS film	
	Excited State	Φ_{PL}
H, Cz	MLCT	$< 10^{-3}$
Nϕ_2	ICT	0.38

T$_1$ Geometries



C-Au-N ~ 120°



C-Au-N = 180°

- Initial thought was that steric interactions were required to maintain linear structure and high F_{PL}.
  (WRONG)
- The key is to avoid MLCT excited state and the Renner-Teller distortion it comes with.

USC

T.Y. Li, *et al.*, *JACS*, **2020**

Summary

- WOLED: lots of ways being investigated
  - High efficiency and color quality: harvest **ALL** excitons
  - Need platforms with long operational lifetime, which requires long lived blue
  - Operational lifetime of blue OLED is enhanced by short radiative lifetime

- Copper, Silver and Gold may compete well with iridium
  - High efficiency, high radiative rate
  - Easily color tunable
  - Very small S_1/T_1 gap
  - OLED lifetime: coming, we need to rethink host and transport materials