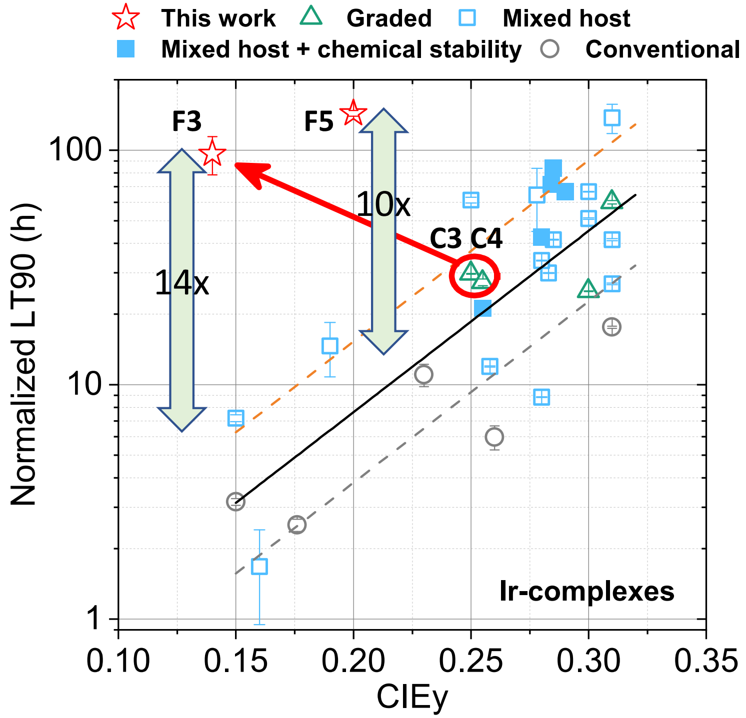
Increasing the Radiative Rates of Triplet Emitters to Achieve Long-Lived and Efficient White-Emitting OLEDs



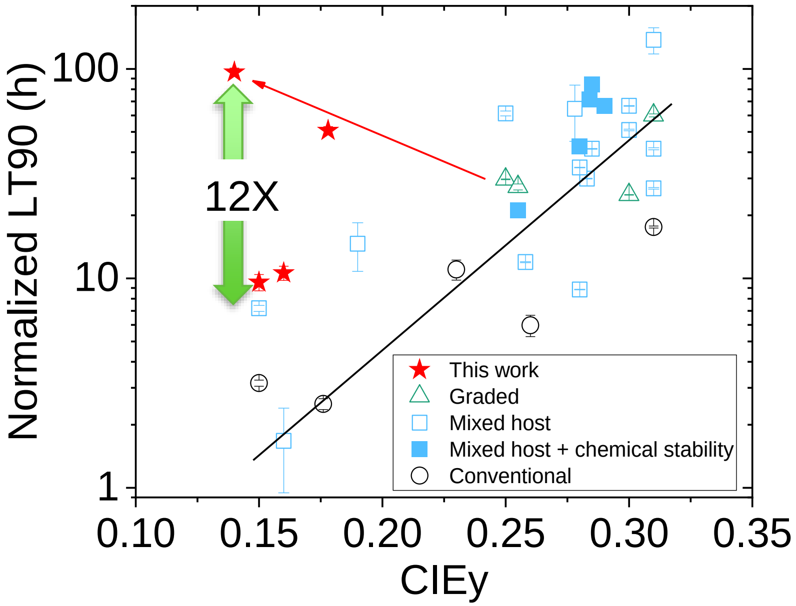
University of Michigan / University of Southern California
Stephen R. Forrest, Professor of Electrical Engineering and Computer Science, Physics and Materials Science and Engineering / Mark E. Thompson, Professor of Chemistry
Tel: (734)647-1147 email: stevefor@umich.edu
Tel: (213)740-6402 email: met@usc.edu

DE-EE0009688

Project Summary

Objective and outcome

- Use a combination of optical engineering and chemistry, with the objective to achieve white OLEDs with internal efficiencies of 100%, and lifetimes exceeding T_{80} = 50,000 h.
- Significantly increase the operational lifetime of blue phosphorescent and TADF OLEDs by developing by decreasing their radiative lifetimes via molecular and cavity designs: i.e. creating optical environments that reduce the lifetime by coupling of the OLED optical modes with the excitonic state.
- Decreasing the radiative lifetime decreases their density in the emission zone, thereby decreasing destructive and fundamental triplet annihilation events.



Team and Partners

University of Michigan: Program PI (S. Forrest) and DOE Technical POC. Tasks: OLED structure design to enhance radiative recombination of phosphor and TADF-based devices

University of Southern California: Subcontractor (M. Thompson); Develop new TADF and Ir-complexes with lifetimes < 1 μs.

Stats

Performance Period: 10/1/21 – 9/30/24

DOE budget: $2,249,996, Cost Share: $578,843

Milestone 1: PF = 3 increases blue PHOLED lifetime

Milestone 2: Blue cMa with $t_{TADF} \leq$ 300 ns

Milestone 3: WOLED w/T_{70} = 50k h at L_0=3000 nits

Problem

- OLEDs provide an exceptional opportunity for lighting due to their simplicity, very high efficiency, color tunability, and adaptability to the widest range of architectural needs
  - 150 lm/W
  - The device IS the luminaire
  - CRI and CCT adjustable across the entire Planckian locus

- 100% efficient (internal), phosphorescent OLEDs have extraordinary stability in the red and green (~500K– 1M hr), but blue lifetime only ~ 100's of hours
  - Ultimately, blue limits the efficiency or lifetime of white phosphorescent OLED (WOLED) lighting
  - Current fix: Use R and G phosphorescent elements and B fluorescent elements to complete spectrum but with loss of efficiency.

Alignment and Impact

- Project is aligned with the goal of reducing energy use intensity in buildings by 30% by 2035
  - OLED efficiencies of 150 lm/W demonstrated but requires all phosphorescent and/or thermally activated delayed fluorescent (TADF) emitters across the spectrum
  - DOE lifetime goal of LT70 = 50 khr is target for WOLED light source in this program, along with potential for 100% internal efficiency
  - Our group has determined cost of WOLED lighting is 50% higher than LED lighting
    - Numerous niche applications for building lighting from diffuse, color tunable, flexible and conformable, architecturally attractive WOLED fixtures.
- Success Metrics
  - Extend lifetime of blue PHOLEDs and TADF molecules by 3 – 5X using cavity effects and molecules with radiative times < 300 ns.
  - Demonstrate WOLEDs based on the solutions found for blue with extended lifetime approaching LT70 = 50 khr

Greenhouse gas emissions reductions

50-52% reduction by 2030 vs. 2005 levels

Net-zero emissions economy by 2050

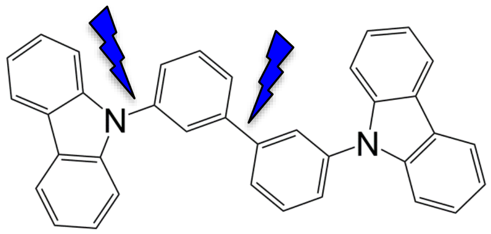
Increase building energy efficiency

Reduce onsite energy use intensity in buildings 30% by 2035 and 45% by 2050, compared to 2005

Reduce the cost of decarbonizing key building segments 50% by 2035 while also reducing consumer energy burdens

Molecular Degradation Is Energy Driven

- Lifetime of OLEDs: R>G>B
- Implication: Device death is energy driven

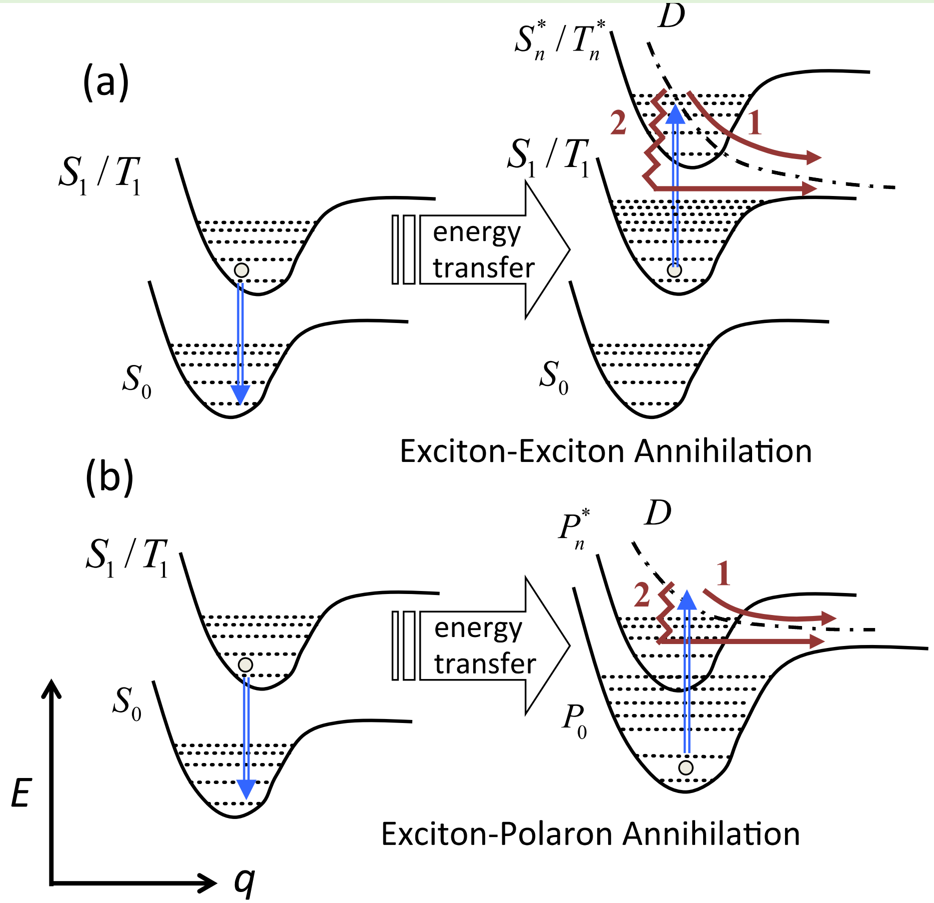


Bond	BE(eV)	Bond	BE(eV)
C-C	3.64	N-N	1.69
C-H	4.28	N-O	2.08
C-O	3.71	N-H	4.05
C-N	3.04	O-O	1.51
C-F	5.03	H-H	4.52

Bond cleavage
Broken bonds → Defects!

Energy Scale
Red light: ~ 2 eV
Green light: ~2.3 eV
Blue light: ~ 2.9 eV

TTA & TPA: Sources of Blue Degradation



Triplet energy (~2.9 eV) + polaron (~3.3 eV) = hot polaron (≥ 6 eV)
More than enough instantaneous energy to break molecular bonds

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

Routes to Increasing Blue PHOLED Lifetime

All routes require reducing triplet density

- Reduce exciton density by **reducing exciton lifetime**

Probability that triplet annihilation will result in molecular bond dissociation:

$$P_{TPA} = \frac{3K_X}{k_r 4\pi r^3} = \frac{3K_X}{k_{r0} 4\pi r^3 PF}$$

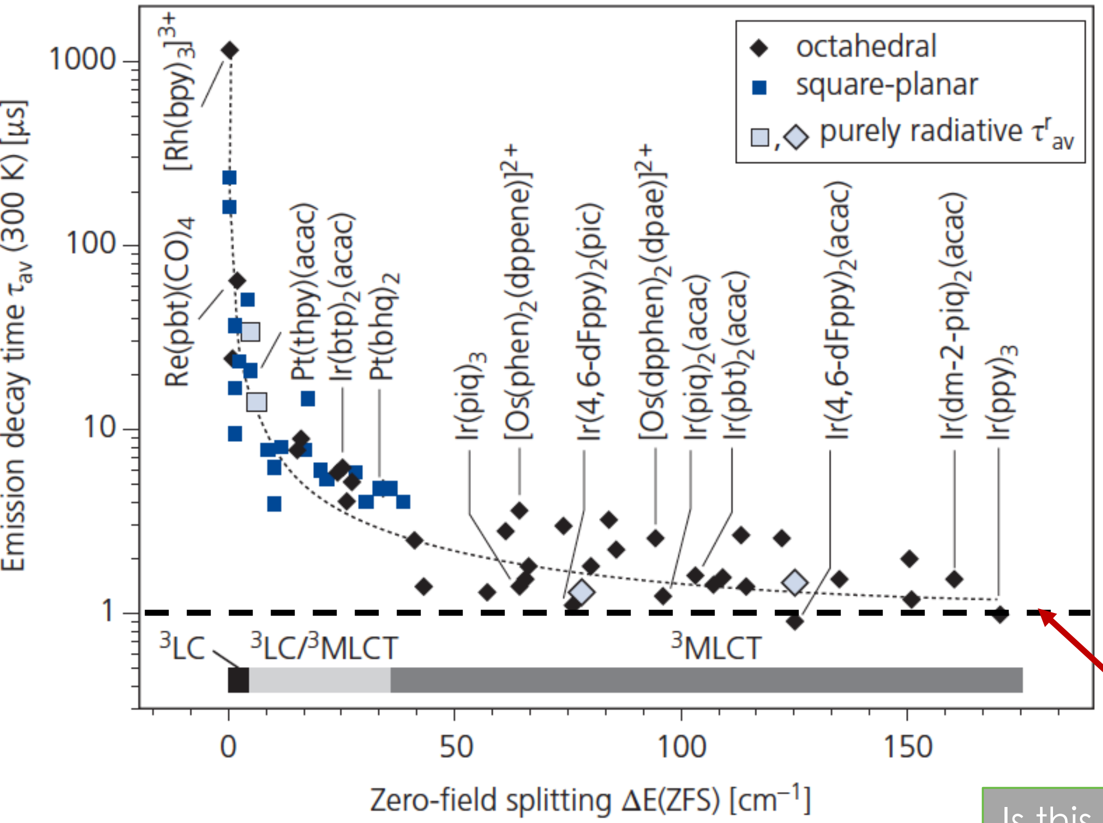
K_X = Defect formation rate; $k_r = k_{r0}PF$; *PF = Purcell factor*

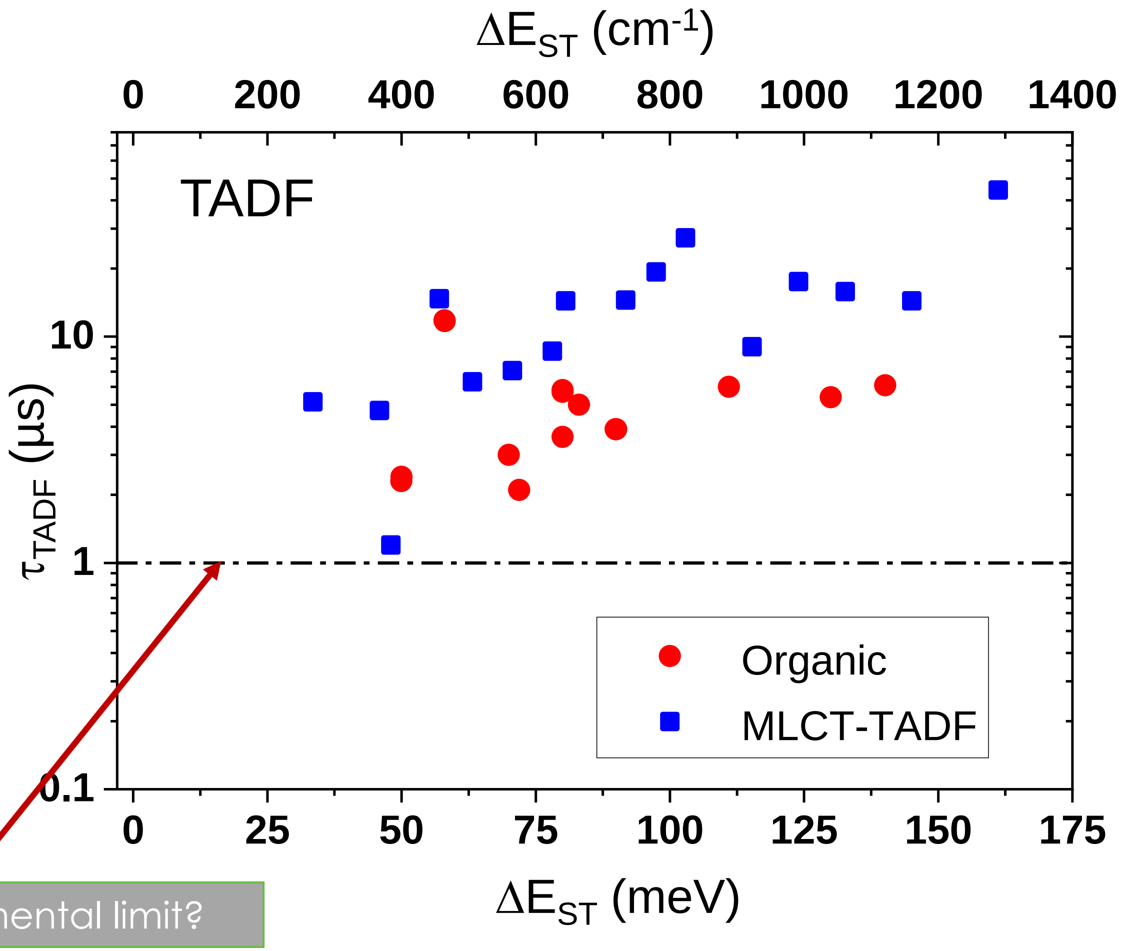
Does the probability for defect creation scale as 1/PF or $1/PF^2$?

- **Enlarge the recombination zone:** EML Grading, Multi-stacked OLEDs
- **Increase outcoupling efficiency:** Numerous effective solutions
- **Decrease the radiative lifetime:** **This Program**
  - Modify the optical environment via cavity effects
  - Modify the emitter structure via metalorganic TADF molecules

Reducing lifetime via Molecular Design

Phosphors





Is this a fundamental limit?

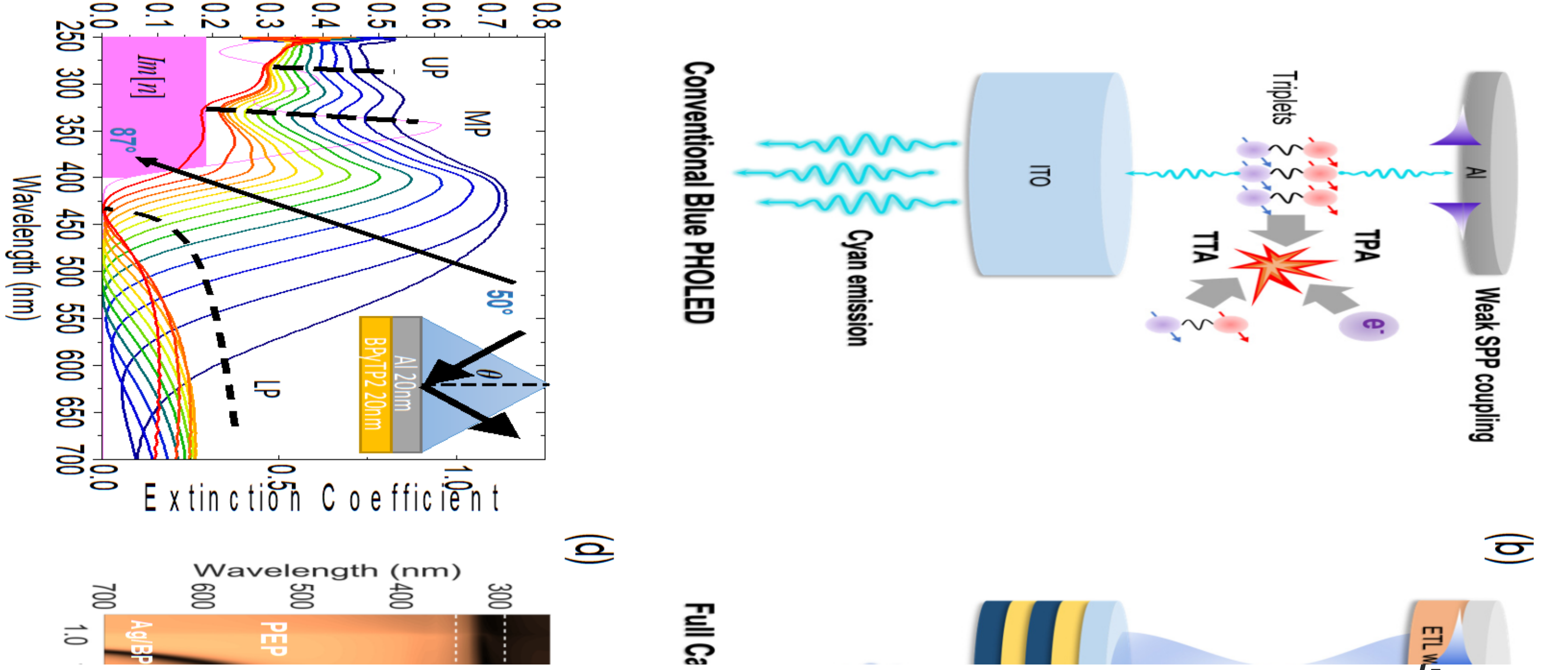
Yersin, et al., Coord. Chem. Rev., **2011** 255, 2622

Liu, Y., *et al. Nature Rev. Mat.*, **2018**

Copper: R. Czerwieniec, *et al., Coord. Chem. Rev.* **2016**

Approach 1: Reduce Radiative Lifetime by Cavity Effects

- **Purcell effect: The enhancement of a quantum system's spontaneous emission rate by its environment.**

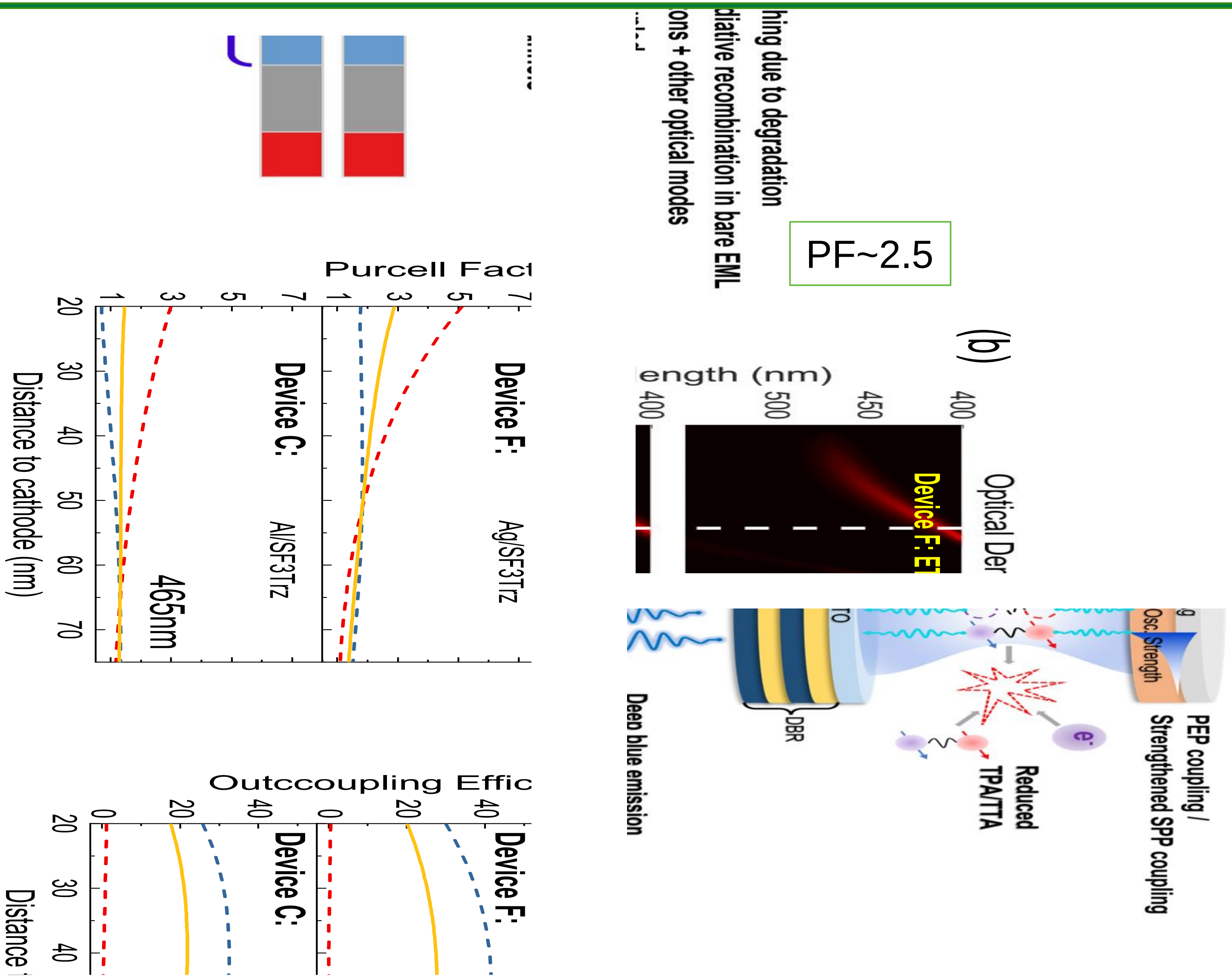


- Optical density of states gives the Purcell Factor: $\mathrm{PF} = \dfrac{k}{k_0} = \dfrac{\rho(\boldsymbol{r}_0,\omega)}{\rho_0(\boldsymbol{r}_0,\omega)}$,
- For efficient emitters, reducing the probability of destructive TTA and TPA by:

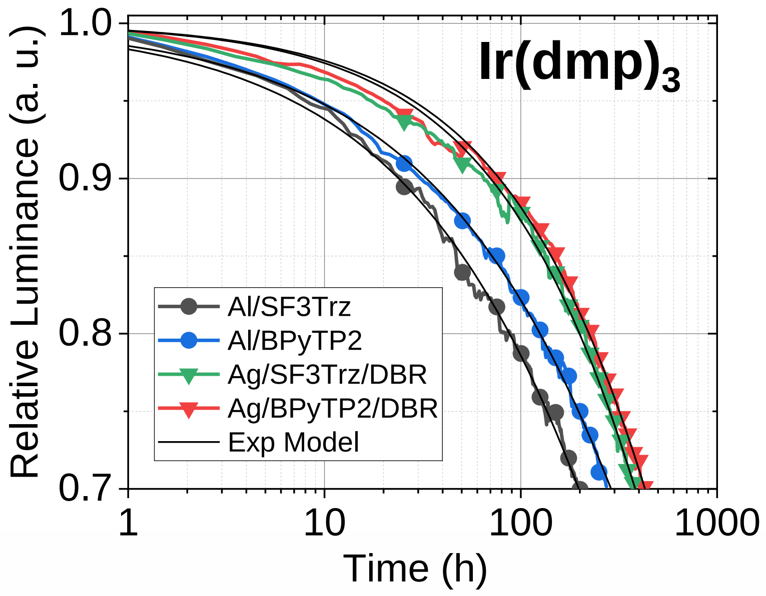
$$P_{TPA} = \frac{3K_X}{k_r 4\pi r^3} = \frac{3K_X}{k_{r0} 4\pi r^3 PF}$$

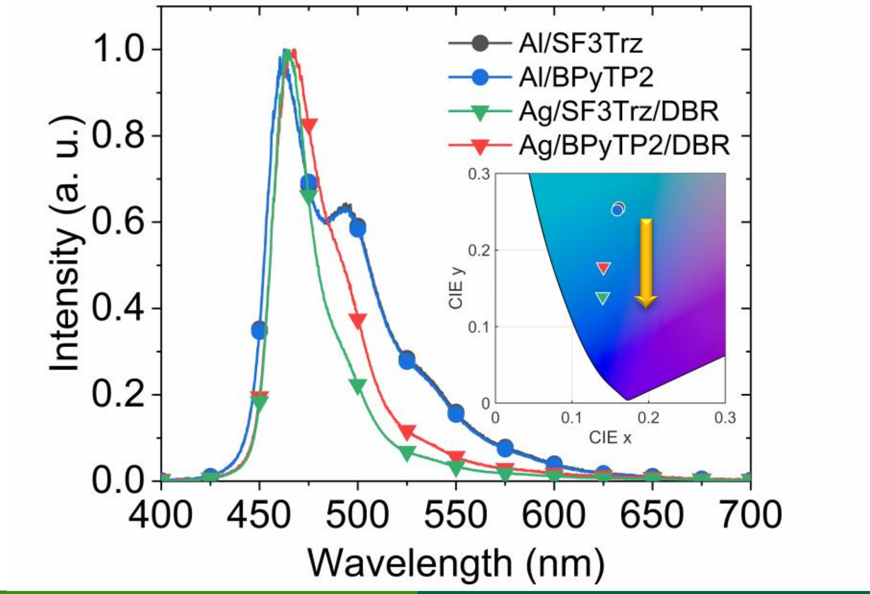
Plasmon-Exciton-Polariton (PEP) Strong Coupling Enhances Lifetime Beyond PF

Introduced PEPs
- Breaks competition between EQE and device lifetime of PF
- Strong coupling depends on both the ETL & cathode

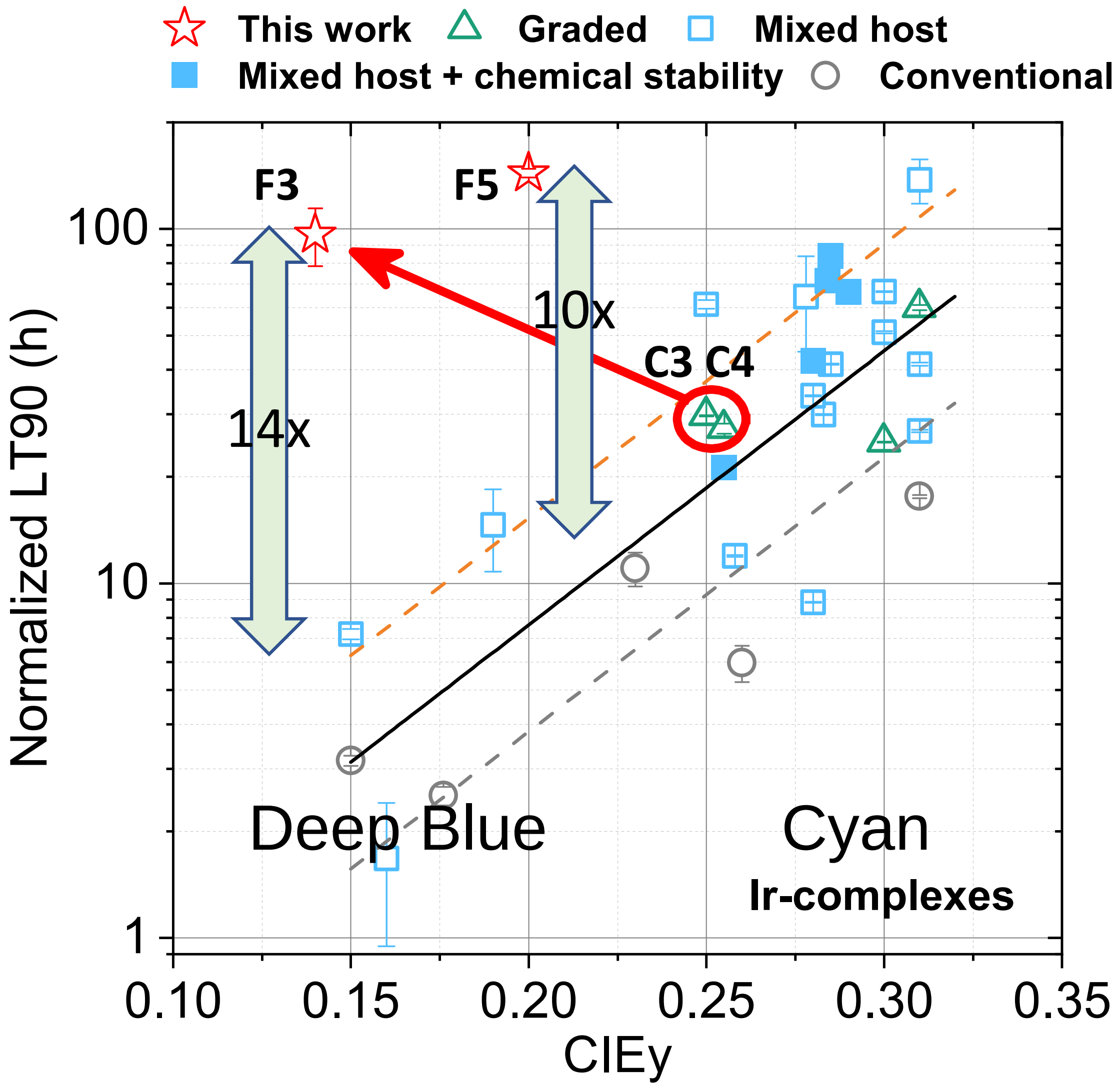


Unexpectedly Large Deep Blue Lifetime Enhancement

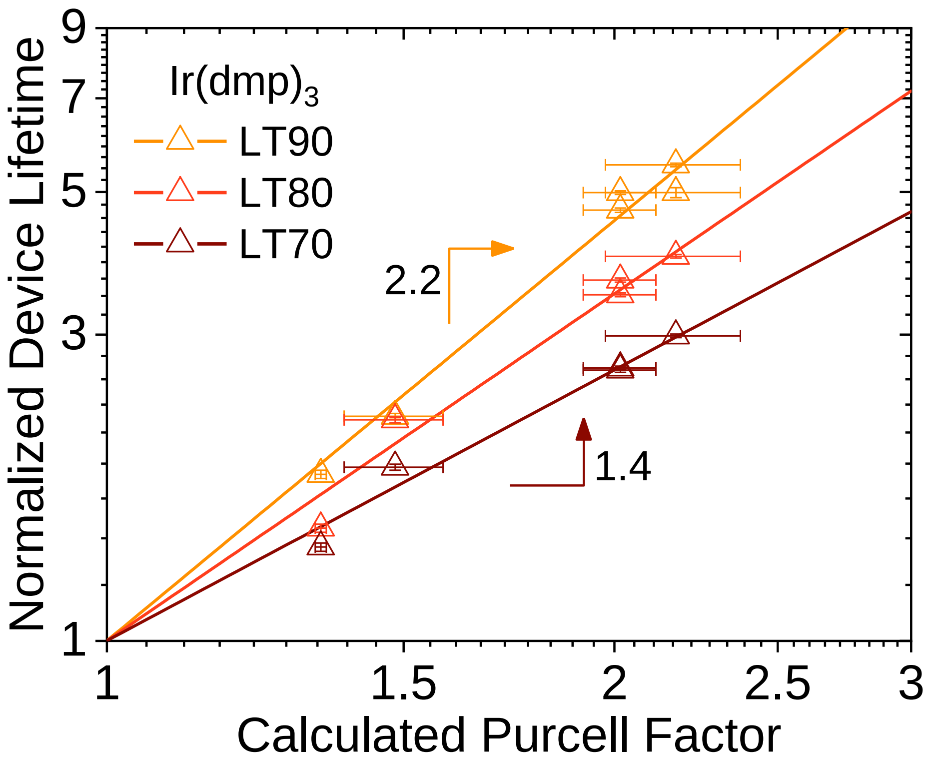




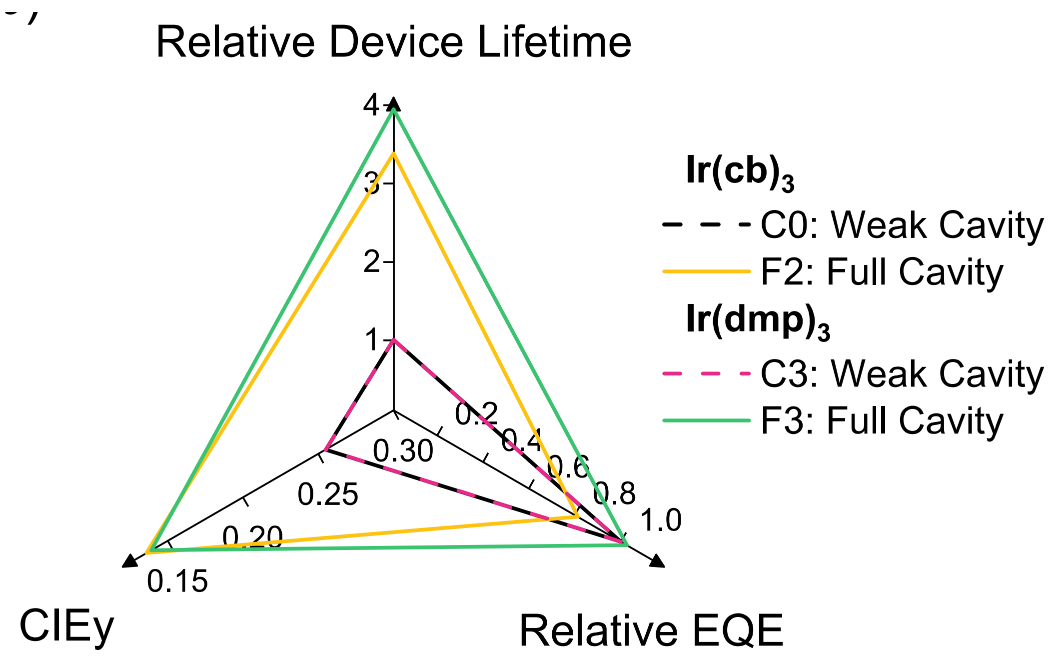
PF ~ 2.5 For F3 PHOLEDs



Lifetime Improvement Scales as PF^n, n = 1.4 – 2.2



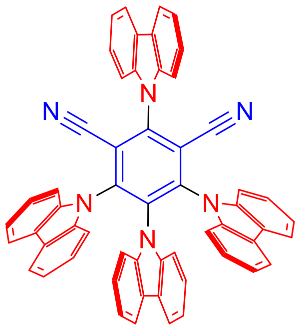
Exponent decreases with time as more dopants converted into defects



Little or no loss in EQE at 4X Lifetime Increase when Plasmon-Exciton-Polaritons Employed

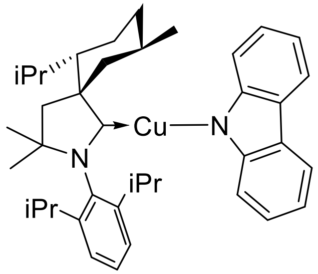
Approach 2: Decreasing Triplet Lifetimes via Molecular Design

- **Organic approach to thermally assisted delayed fluorescence (TADF)**

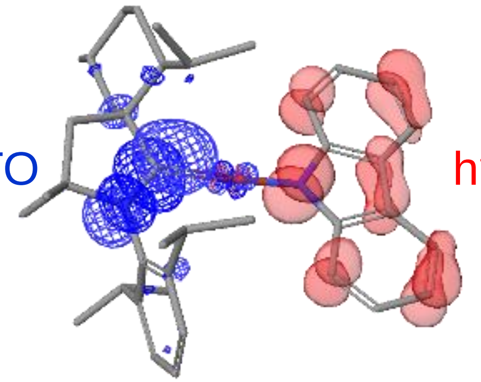


  - Prepare molecules where the **donor** is approx. orthogonal to the **acceptor**
  - If $\mathbf{D^{+}}$ and $\mathbf{A^{-}}$ are orthogonal: $S_1 = T_1$ in energy
  - Very small ΔE_{ST} but also small oscillator strength for S_1 ("fluorescence" of TADF)

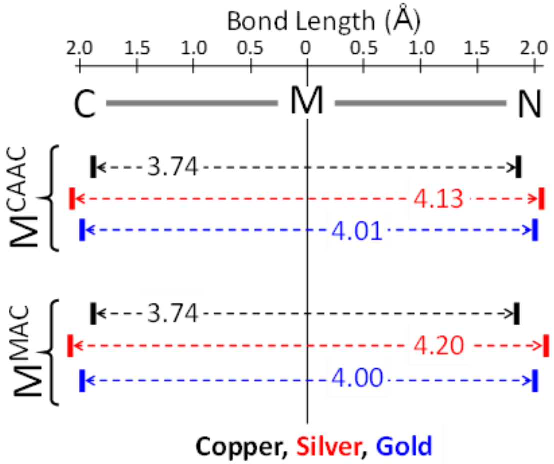
- **Inorganic approach**
  - Keep **donor** and **acceptor** aligned, but space them apart
  - Minimal metal participation in CT



e^{-}NTO

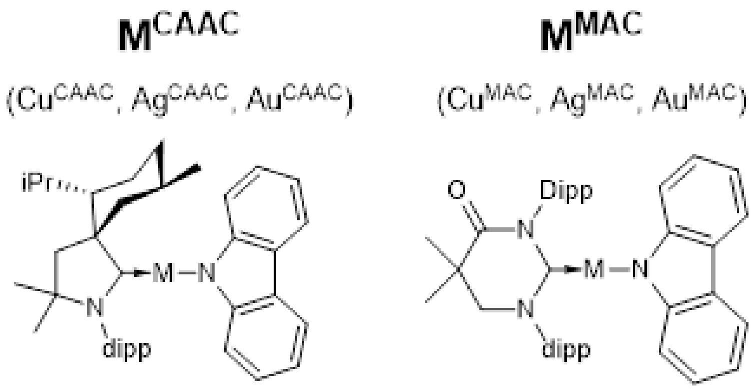


h^{+}NTO



Two TADF Design Approaches Lead to Unprecedented Emission Rates

(carbene)MCz



dipp = 2,6-di-isopropylphenyl

Blue Emission

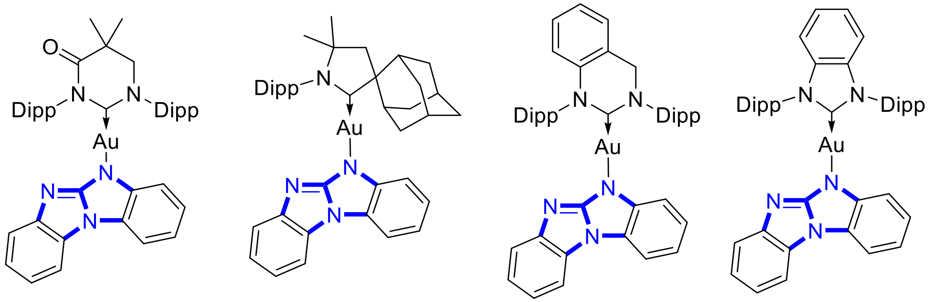
	Φ_{PL}	τ (μs)
Cu	1.0	2.8
Ag	1.0	0.5
Au	1.0	1.1

Green Emission

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

R. Hamze, *et al.*, *J. Am. Chem. Soc.*, **2019**, *141*, 8616

π-Extended Amide Donor



	Room Temperature in polystyrene			
	λ (nm)	Φ_{PL}	τ (μs)	k_r^{TADF} (10^6 s^{-1})
MAC	506	0.90	0.4	2.3
CAAC	476	0.95	0.55	1.7
BZAC	452	> 0.95	0.28	3.7
BZI	429	> 0.95	0.25	4.0

New amide gives the highest k_r^{TADF} reported

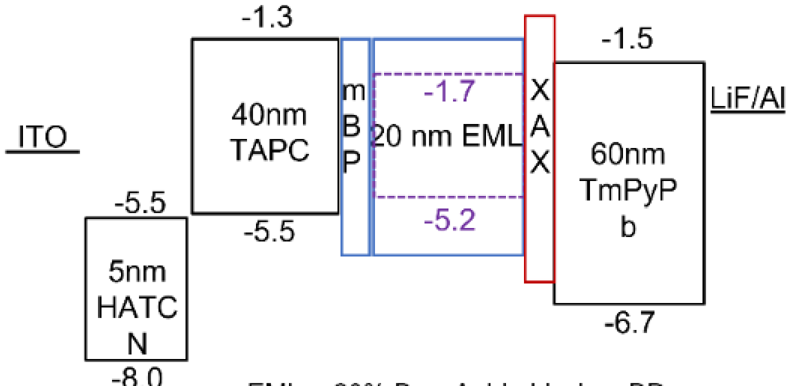
– Fastest triplet-controlled emitters reported

Why are they so fast?

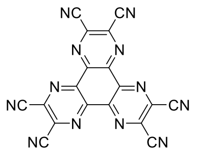
– Small ΔE_{ST} without a decrease in k_{S_1}

C. Muniz, *et al.*, *J. Am. Chem. Soc.*, **2022**, *144*, 17916

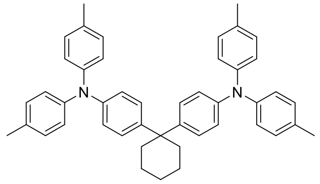
Au_{bim}^{BZAC} OLED: Early Result From UM and USC



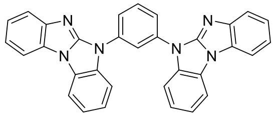
EML = 20% BzacAubimbim in mBP



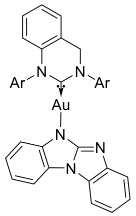
HATCN



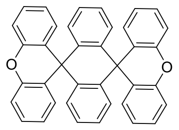
TAPC



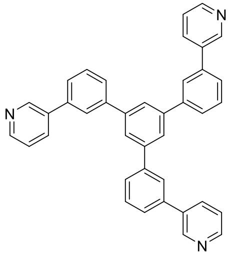
mBP



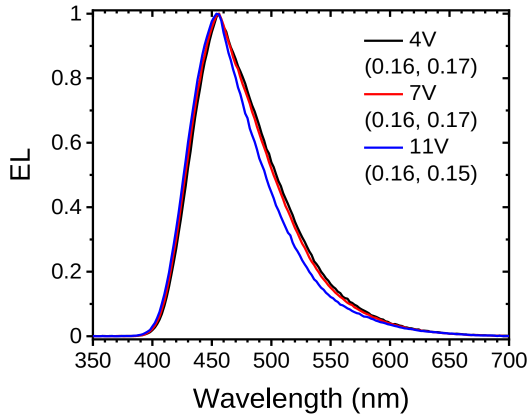
BzacAubimbim

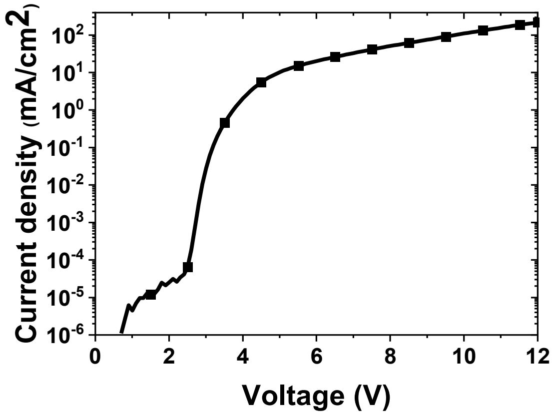


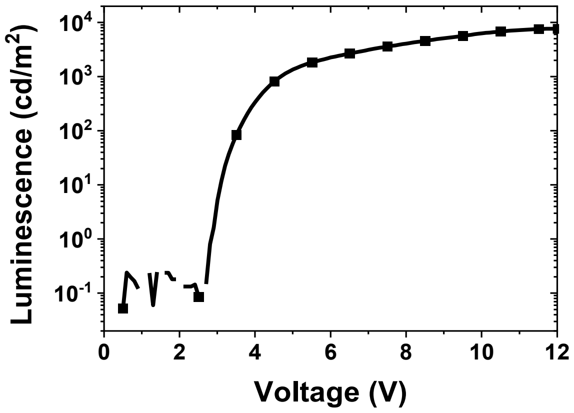
XAX

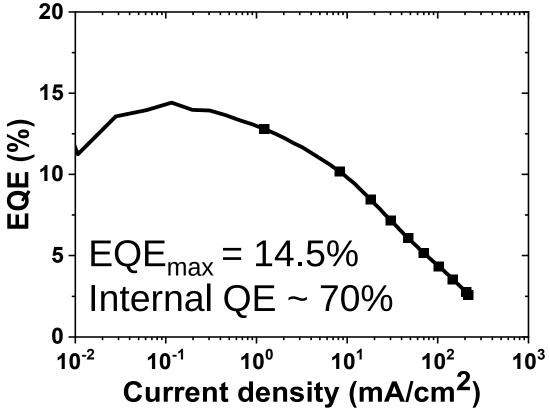


TmPyPB









- XAX is not morphologically stable
- Developing new host materials for testing deep blue OLEDs

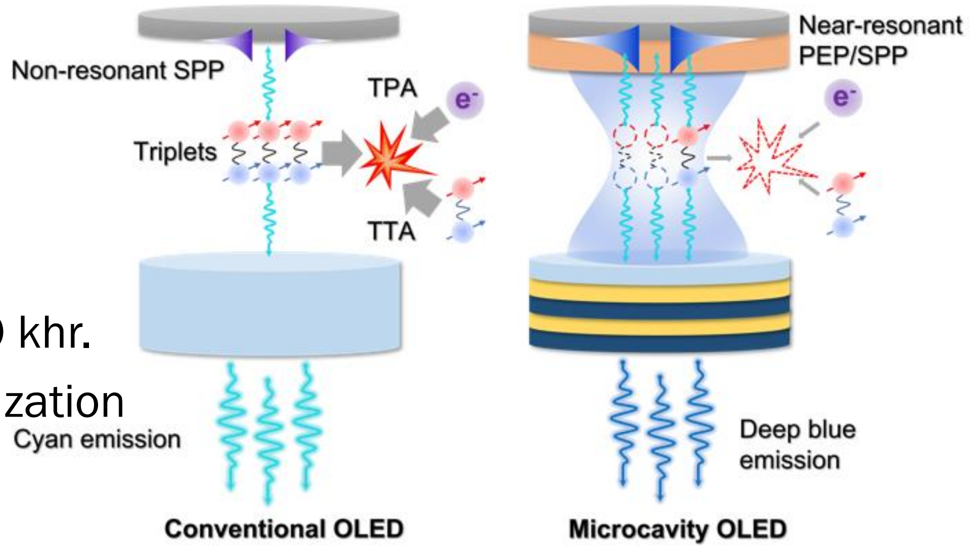
Progress and Future Work

Progress

- **Observed PF = 3 meeting goals ✓**
- **Demonstrated a new class of 100% PLQY metalorganic TADF molecules with trad < 300 ns exceeding goals ✓**
- **Discovered the plasmon-exciton-polariton effect for increasing device lifetime beyond PF ✓ ✓ ☆**
  - Allows engineering cavities to independently optimize color, EQE and lifetime of PHOLEDs
  - Observe >14X *relative* increase in lifetime compared to other deep blue Ir-complex based OLEDs
  - Observe 4X *absolute* lifetime improvement of control cyan PHOLED lifetime exceeding goals

Next Steps

- **Employ short radiative lifetime TADF molecules in PEP cavities**
  - Determine coupling to singlet/triplet TADF manifolds
  - Demonstrate stable, 20% EQE TADF OLED operation
  - Demonstrate long-lived WOLEDs with PEP cavities with lifetimes of 50 khr.
  - Transfer technology and license IP to industrial sector for commercialization



Conclusions

- **The pathway to long lifetime blue emitters controlled by triplets (i.e. both phosphors and TADF) has been long and narrow**
  - Better life through chemistry – every layer of the OLED matters
  - Lower density exciton emission zones
  - Shorter radiative lifetimes
  - Improved outcoupling
  - Coupling to plasmons
- Solving this problem is likely the **single most important challenge confronting organic electronics** (specifically OLED displays) today
- **Blue PHOLED lifetimes are suitable for lighting**
  - Lighter blues, fewer photons/segment required than in displays

Thank You

University of Michigan / University of Southern California

Stephen R. Forrest, Professor of Electrical Engineering and Computer Science, Physics and Materials Science and Engineering / Mark E. Thompson, Professor of Chemistry

Tel: (734)647-1147 email: stevefor@umich.edu

Tel: (213)740-6402 email: met@usc.edu

DE-EE0009688

REFERENCE SLIDES

Project Execution

	FY2022				FY2023				FY2024			
Planned budget	968,301				948,854				911,684			
Spent budget	572,640				78,632							
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Past Work												
M2.1.1 Software - structure optimization												
M2.1.2 Design structures PF>5, EQE>20%												
M2.2.1 Fabricate devices w/increased PF.												
M2.2.2 Fab. PHOLEDs w/PF>5, EQE>20%												
M2.3.1 Lifetest blue PHOLEDs, PF=1 to >3												
M3.1.1 (carbene)M(amide) compounds												
M3.1.2 blue cMa modelling & database												
M3.1.3 Modeling/synthesis acceptor+carbene cMa												
M3.1.4 OLEDs w/cMa emitters												

- ✓ Go/No-Go 1.1 Demonstrate an OLED structure that reaches a PF=3 with concomitant increase in blue emitting device stability
  - *Achieved PF ~ 3 & prolonged device lifetime using Ag-ITO half cavity & Ag-DBR cavity. Lifetime enhancement ranges from 1.5x to 2.6x at the maximum, reaching an extrapolated LT70 = 570hr operating under 10mA/cm^2 current density.*
- ✓ Go/No-Go 1.2 Demonstrate a blue emissive cMa with t_{TADF}<= 300 ns
  - *Two of the four complexes give deep blue emission and have radiative lifetimes (tTADF) < 300 ns*

Project Execution

	FY2022				FY2023				FY2024			
Planned budget	968,301				948,854				911,684			
Spent budget	572,640				78,632							
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Current/Future Work												
M3.2.1 Single strapped cMa												
M3.2.2 Double strapped cMa												
M3.2.3 OLEDs w/macrocyclic cMa												
M4.1.1 Fab. Blue PHOLEDs, PF>5, EQE>20%												
M4.1.2 Fab. Short tTADF molec. in ucavities												
M4.2.2 Determine if increased PF increases tTADF stability												
M4.3.1 Lifetest blue OLEDs												
M4.3.2 Lifetest white OLEDs w/ucavity, graded, T-managed blue												

Task 4 Modifying emission lifetimes of heavy-metal phosphors and binuclear compounds

We determined that the *fac* and *mer* isomers do not have ZFS > ΔE_{st} for $Ir(pmp)_3$. This is not a good system to investigate further.

Go/NO-GO 2.1: Demonstrate an OLED structure that reaches a *PF* > 3; stretch goal *PF* > 5

Project Execution

	FY2022				FY2023				FY2024			
Planned budget	968,301				948,854				911,684			
Spent budget	572,640				78,632							
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Current/Future Work												
M5.1.1 cMa for efficient dopant alignment & OLEDs							■	■	■			
M5.2.1 Blue cMa Janus carbene							■	■	■			
M5.2.2 Strapped Janus cMa							■	■	■	■	■	
M5.2.3 OLEDs w/Janus cMa								■	■	■	■	■
M5.3.1 Blue emissive tandem cMa							■	■	■			
M5.3.2 Macrocyclic blue tandem cMa							■	■	■	■	■	
M5.3.3 OLEDs tandem cMa								■	■	■	■	
M5.4.1 Synthesis & photophysics of ZFS-F emitters							■	■	■			
M5.4.2 OLEDs with ZFS-F emitters								■	■	■	■	

- End of Program: WOLED w/LT70=50 kh at L_0=3000 nits

Team

•Team and Partners

•University of Michigan: Program PI (S. Forrest) and DOE Technical POC. Tasks: OLED structure design to enhance radiative recombination of phosphor and TADF-based devices

•University of Southern California: Subcontractor (M. Thompson); Develop new TADF and Ir-complexes with lifetimes < 1 μs.

Key Stakeholder

•Universal Display Corp.: Contact: Dr. Mike Hack. Licensee of UM & USC IP and commercial supplier of OLED technology and materials.