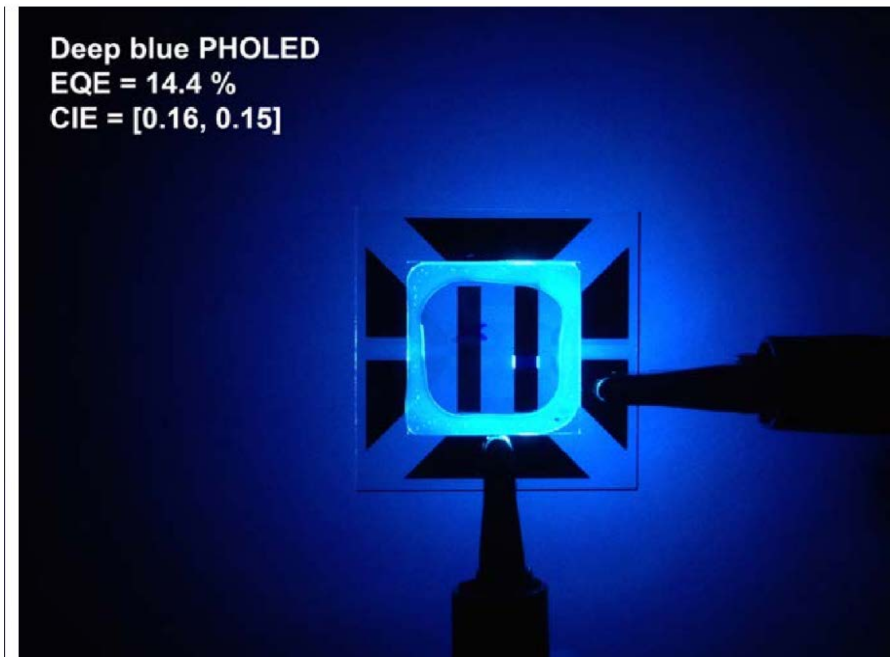
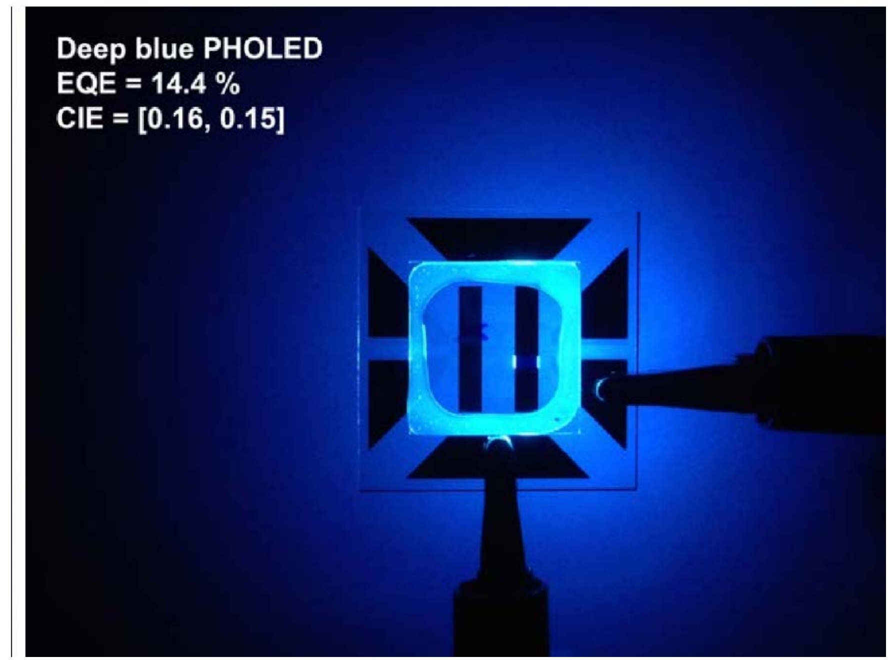
# Stable, high efficiency white phosphorescent organic light-emitting devices (OLED) by reduced molecular dissociation

2017 Building Technologies Office Peer Review

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University of Michigan

# Project Summary

**Timeline**:

Start date: September 1, 2015

Planned end date: August 31, 2017

Key Milestones

1. Demonstrate a graded *blue* PHOLED (CIE=0.15, 0.31) in single element or stack with an EQE >15%, $LT_{70}$ > 3,000 hr at $L_0$=1000 nits. - FY2016
2. Demonstrate that introducing an excited state sink into a blue PHOLED can extend its lifetime 2X, showing proof of concept. – FY 2017

**Budget**:

**Total Project $ to Date**:

- DOE: $617,989
- Cost Share: $217,131

**Total Project $:**

- DOE: $1,314,241
- Cost Share: $433,397

**Key Partners**:

| |
|---|
| University of Southern California, Mark Thompson, PI |
| Universal Display Corporation, Mike Hack, PI |

**Project Outcome**:

Pursuing radically new strategies for increasing the lifetime of blue phosphorescent light emitting devices (PHOLEDs).

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# Purpose and Objectives

**Problem Statement**: Increase the lifetime of blue PHOLEDs to ultimately achieve the MYPP goal for white OLEDs of T70 = 50,000 hr at $L_0$ = 3000 nits.

**Target Market and Audience**: The target market is the OLED lighting industry which currently is very small. With success in extending lifetime and lower cost per lumen, OLEDs can dominate area lighting applications.

**Impact of Project**: Success will provide the catalyst to launch OLEDs as a large new energy saving and environmentally friendly form of solid-state lighting.
OLED lighting products are now entering the marketplace with good efficiencies (60-80 lm/W) and at high price points (~$2K/m$^2$), but with improvements in lifetime, both of these metrics will significantly improve.

1. Project output: Long lived blue and white OLEDs with the blue component targets of T70 = 3000 hr at $L_0$ = 1000 nits and 15% EQE.
2. Near-term outcomes (during or up to 1yr after project): Meet WOLED MYPP metrics stated above.

# Approach

Systematically seek robust **dopant** and **host** molecular pairs whose energy gaps allow high efficiency blue PHOLEDs

Introduce "excited state sinks" co-doped with the host and phosphor in the EML to drastically reduce the lifetime of multiply-excited triplets and/or charge carriers. ***Excited state sinks represent an entirely new approach to extending OLED lifetime.***

Implement stacked white emitting PHOLEDs to decrease the drive current while maintaining high efficiency.

**Key Issues**: Determine routes for molecular dissociation to develop are more robust managers and emission layer materials sets than currently available.

**Distinctive Characteristics**: Employing hot state managers to totally bypass dissociative reactions in blue PHOLEDs is completely original and strikes at the most fundamental mechanisms leading to degradation.

# Progress and Accomplishments (I)

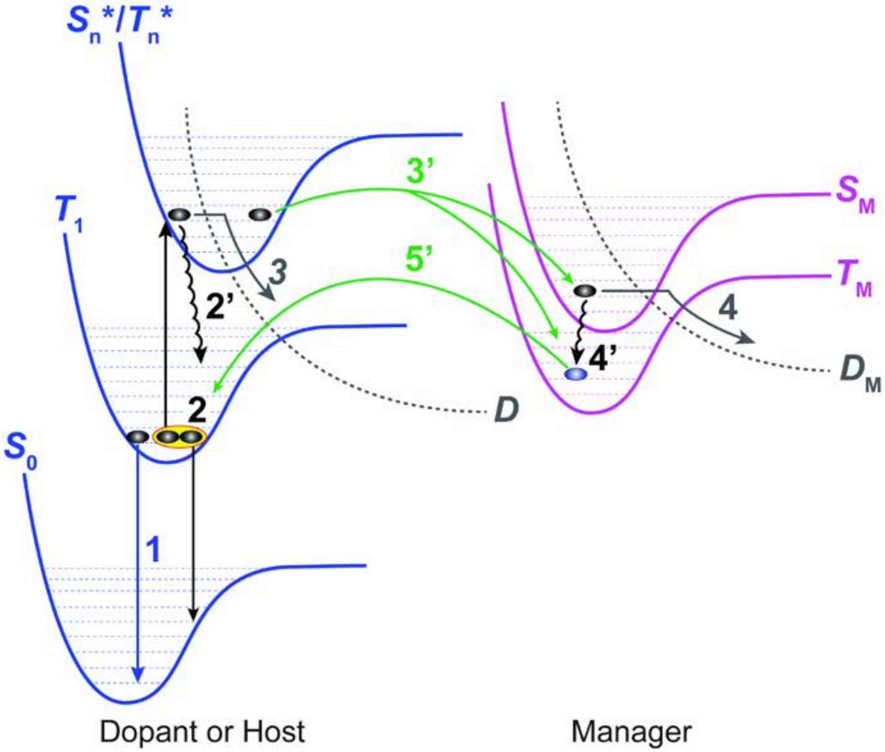
Clearly demonstrated the efficacy of managers to reduce dissociative reactions and significantly improve blue PHOLED lifetime.

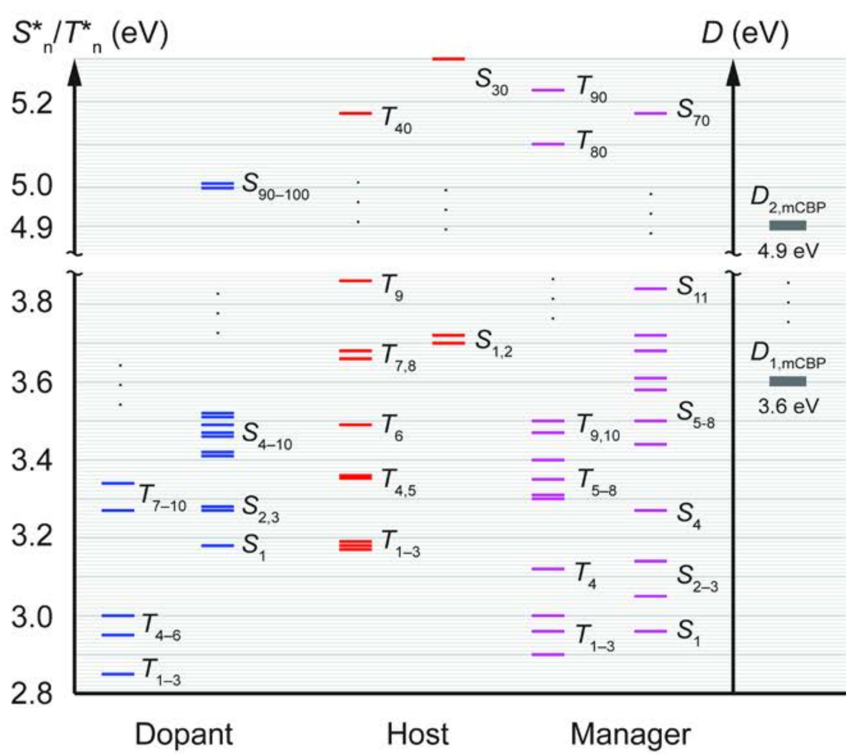
| Device | $J_0$ [mA/cm$^2$] | EQE [%] | $V_0$ [V] | CIE† | LT90 [hr] | T80 [hr] | ΔV(T90) [V] | ΔV(T80) [V] |
|---|---|---|---|---|---|---|---|---|
| **CONV** | 6.7±0.1 | 8.0±0.1 | 6.6±0.0 | [0.15, 0.28] | 27 ± 4 | 93 ± 9 | 0.3 ± 0.1 | 0.4 ± 0.1 |
| **GRAD** | 5.7±0.1 | 8.9±0.1 | 8.0±0.0 | [0.16, 0.30] | 47 ± 1 | 173 ± 3 | 0.6 ± 0.1 | 0.9 ± 0.1 |
| **S0** | 5.5±0.1 | 9.4±0.1 | 9.2±0.0 | [0.16, 0.30] | 71 ± 1 | 226 ± 9 | 0.9 ± 0.1 | 1.2 ± 0.1 |
| **S1** | 5.4±0.1 | 9.5±0.1 | 8.8±0.1 | [0.16, 0.29] | 99 ± 3 | 260 ± 15 | 1.2 ± 0.1 | 1.6 ± 0.1 |
| **S2** | 5.4±0.1 | 9.3±0.0 | 8.9±0.1 | [0.16, 0.31] | 103 ± 0 | 285 ± 8 | 0.7 ± 0.1 | 1.0 ± 0.1 |
| **S3** | 5.3±0.1 | 9.6±0.0 | 9.0±0.1 | [0.16, 0.30] | 141 ± 11 (5.2X) (3.0X) | 334 ± 5 (3.5X) (1.9X) | 1.1 ± 0.1 | 1.5 ± 0.2 |
| **S4** | 5.2±0.1 | 9.6±0.2 | 8.6±0.0 | [0.16, 0.31] | 126 ± 7 | 294 ± 16 | 1.0 ± 0.1 | 1.3 ± 0.1 |
| **S5** | 5.1±0.1 | 9.9±0.1 | 8.6±0.0 | [0.16, 0.31] | 119 ± 6 | 306 ± 3 | 0.9 ± 0.1 | 1.2 ± 0.1 |

# Progress and Accomplishments (II)

Identified aspects of manager molecules required to achieve very long blue PHOLED lifetimes.

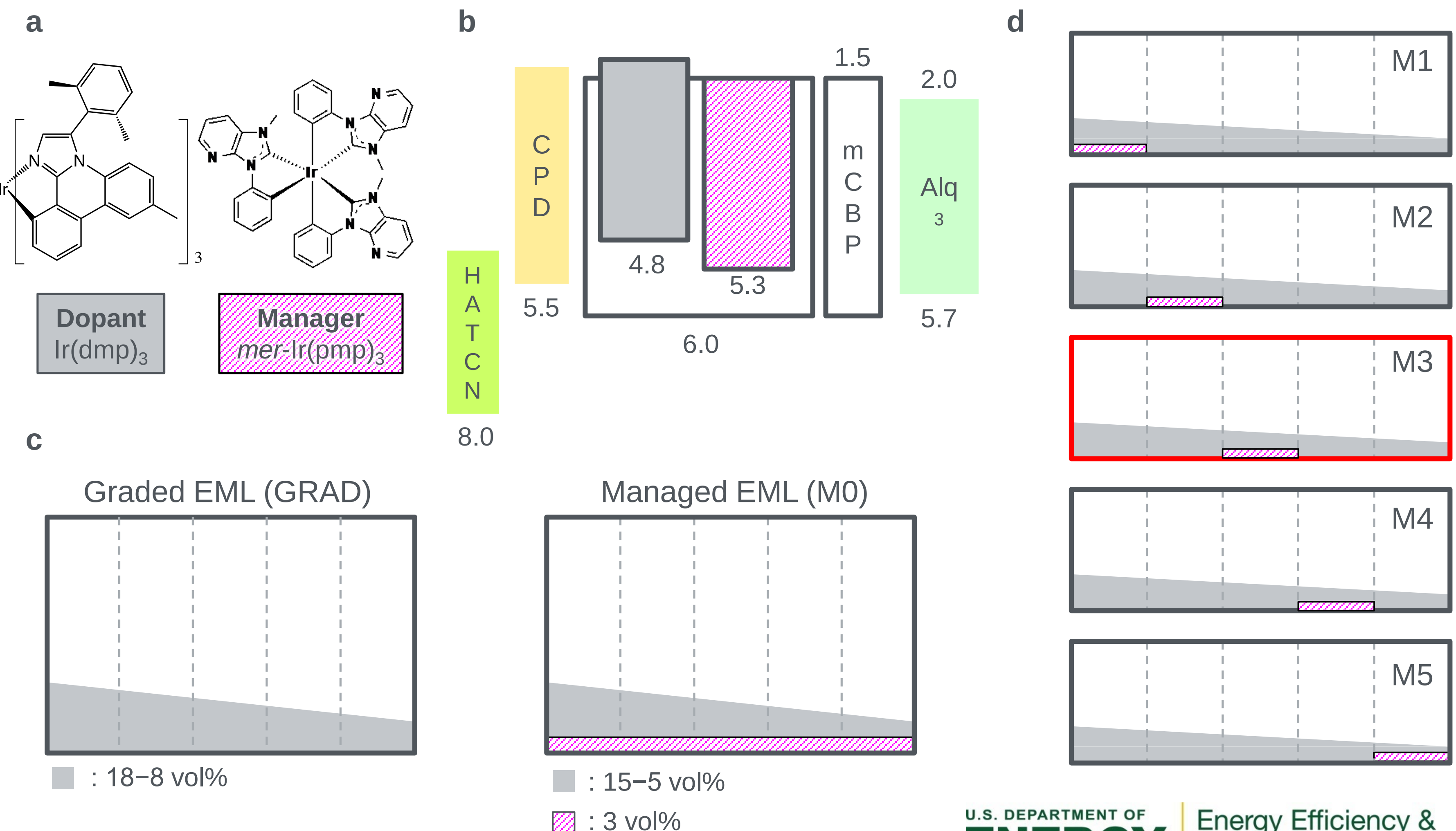
- Triplet (or polaron) energy higher than the lowest triplet of host/dopant ($T_1$) to prevent loss of radiative efficiency
- Sufficient orbital overlap between manager and vulnerable molecule such that transfer rate > dissociation rate of molecule
- Stable manager molecule



# Progress and Accomplishments (III)

Found that managers placed at point of highest exciton density result in longest lived PHOLEDs

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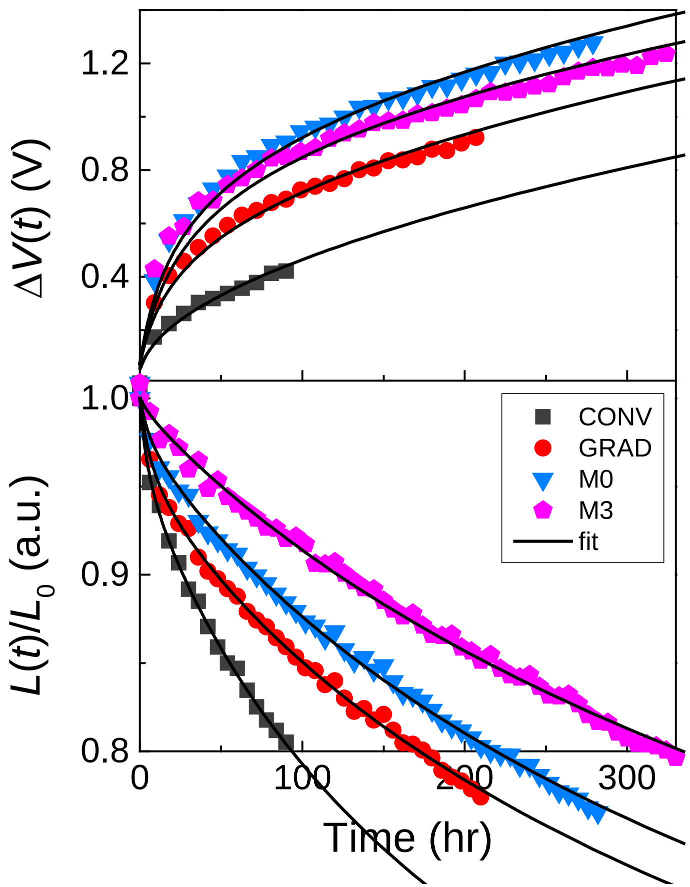
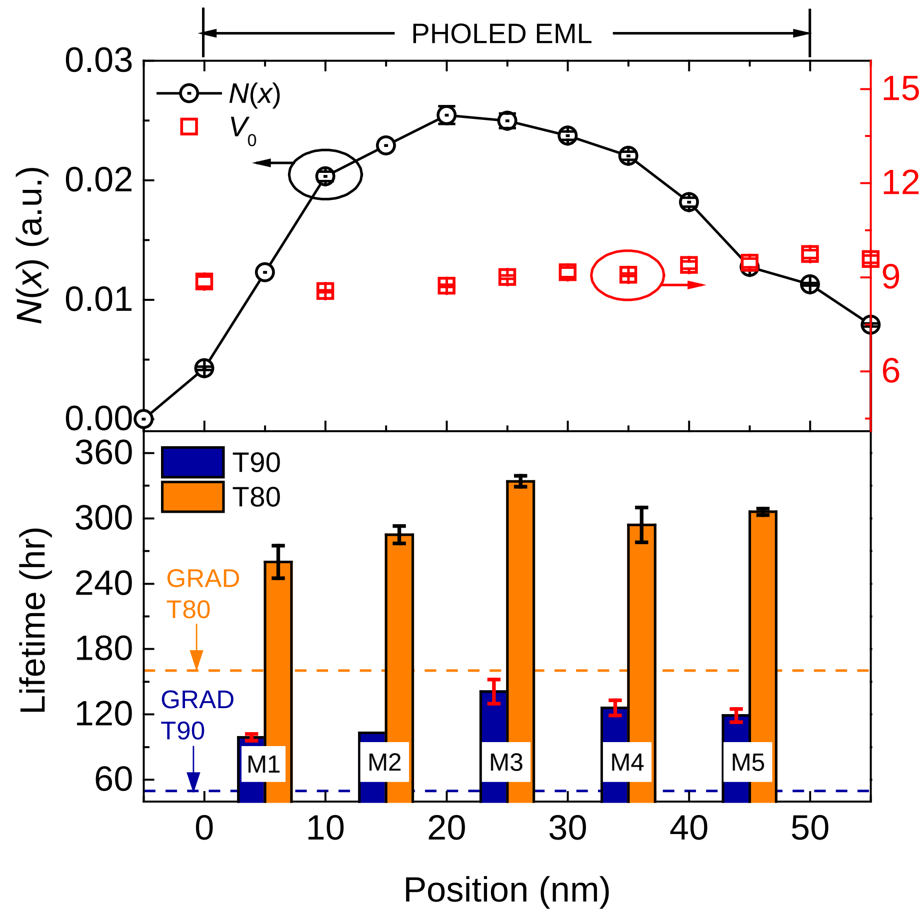
# Progress and Accomplishments (IV)

Triplet annihilation model accurately predicts device lifetime

Measurement of exciton density and device lifetime are consistent

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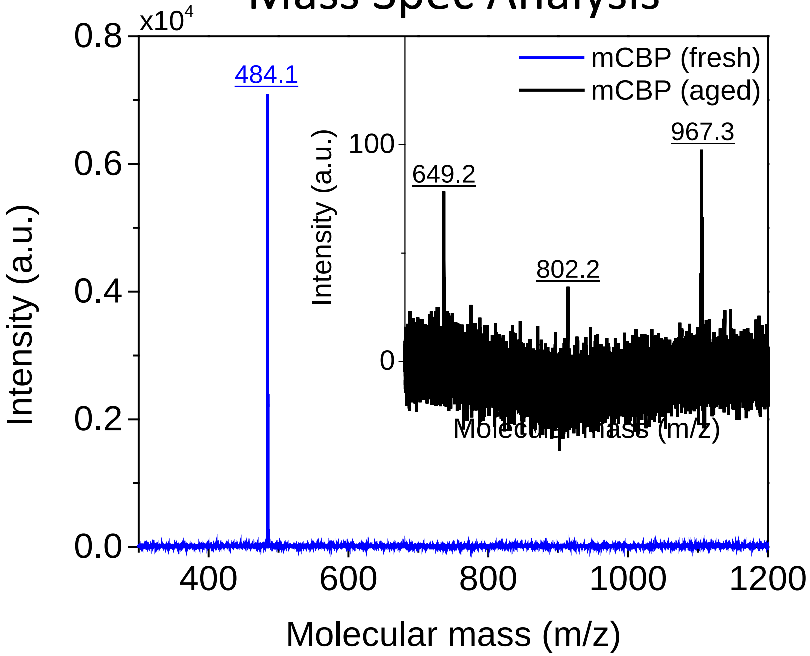
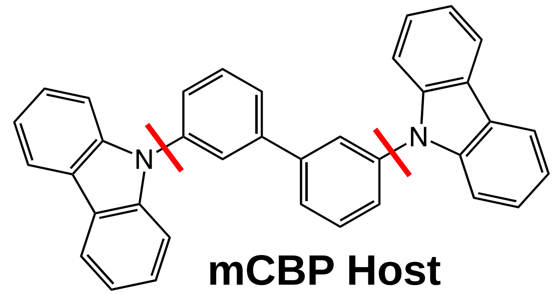
# Progress and Accomplishments (V)

Identified dissociation products due to triplet-triplet annihilation (consistent with model degradation path) in hosts and dopants

Mass Spec Analysis



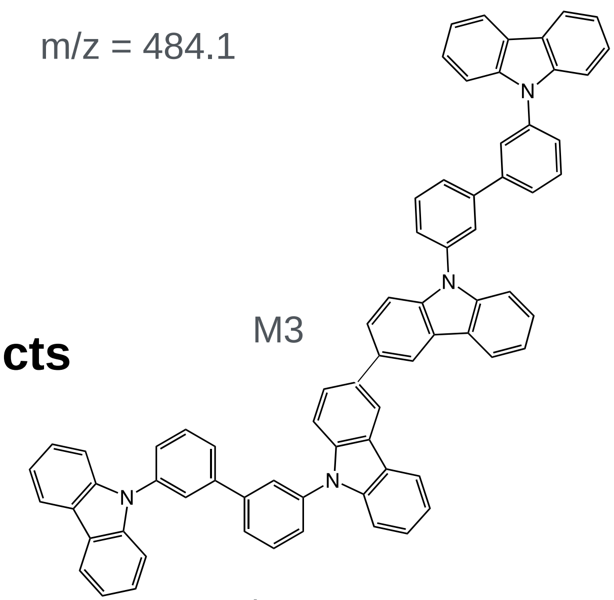




**mCBP Host**

m/z = 484.1

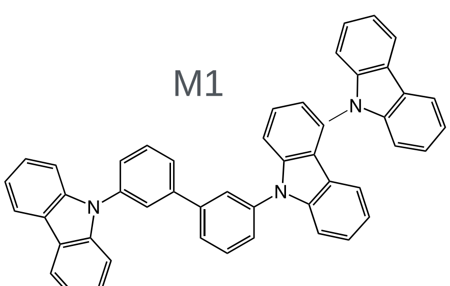
**Degraded products**

M3



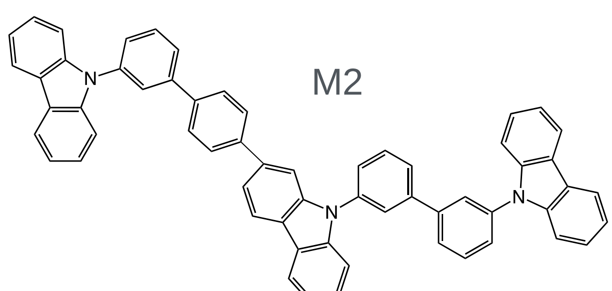
m/z = 967.3

M1



m/z = 649.2

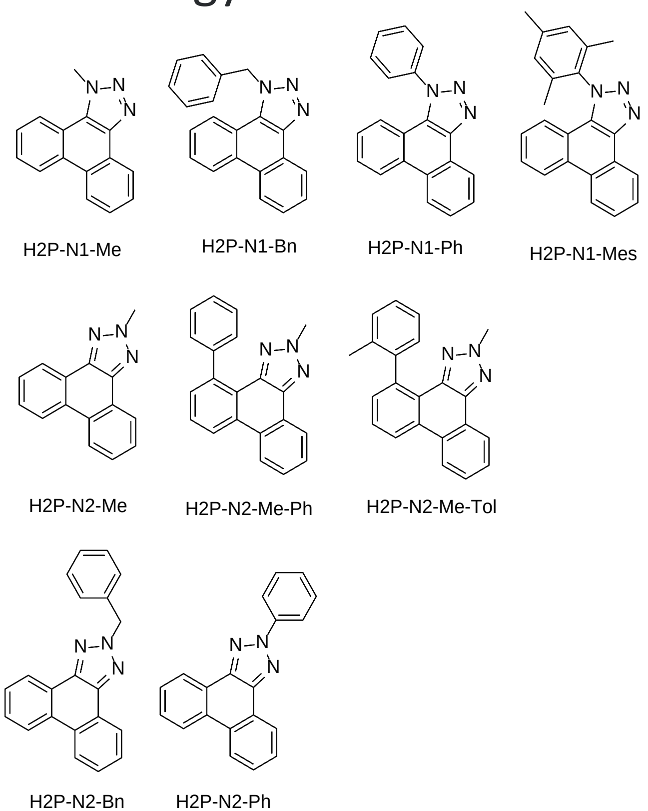
M2

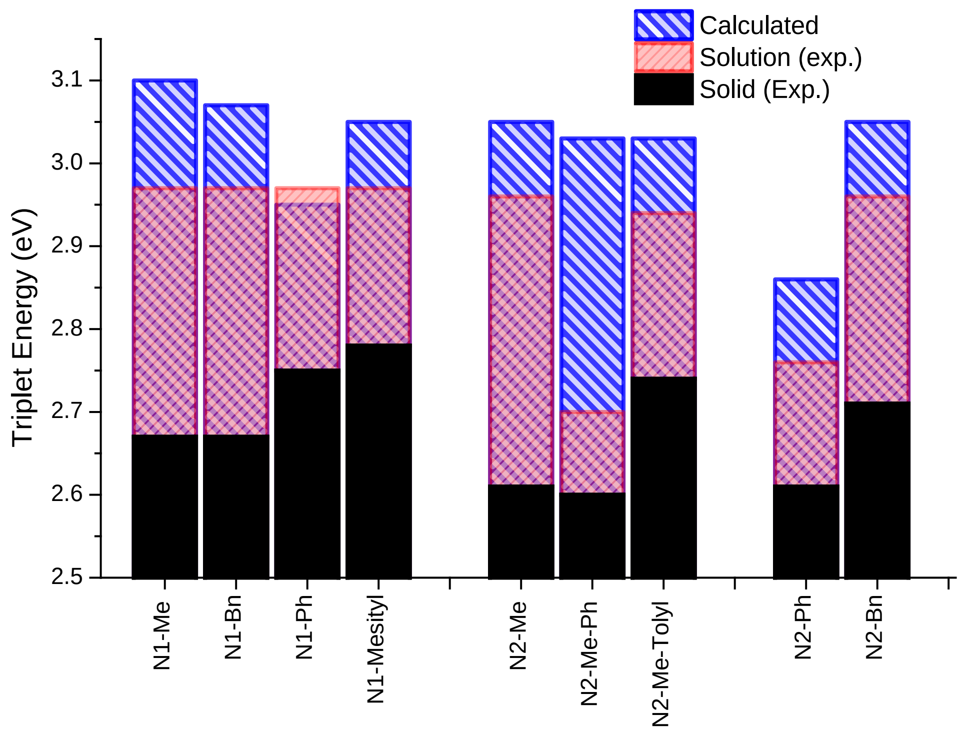


m/z = 802.2

# Progress and Accomplishments (VI)

- Developing new, stable hosts: Triazoles
- Models suggest that tricyclic hosts are more thermally stable and have lower reduction potentials than carbazoles.
- Triazoles give high $T_1$ energies (> 3.0 eV solution and theory)
  - Addition of bulky functional groups to the molecular core increases the triplet energy in solid state



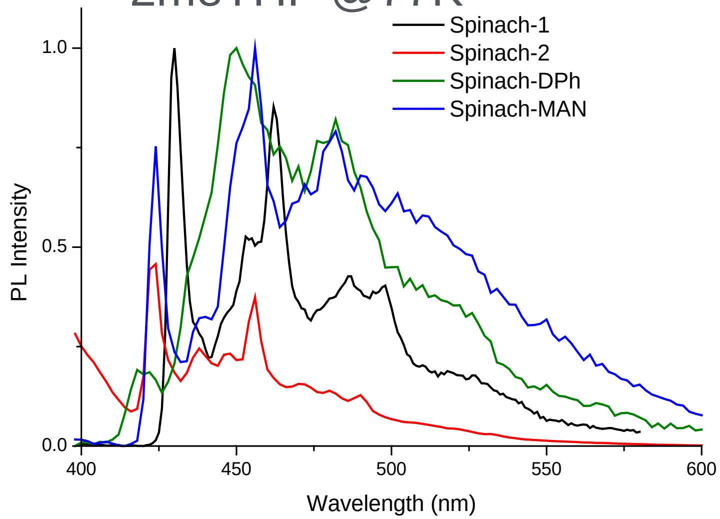
# Progress and Accomplishments (VII)

Spiro INdoloACridine Hosts (SPINACH) developed as alternative robust host system

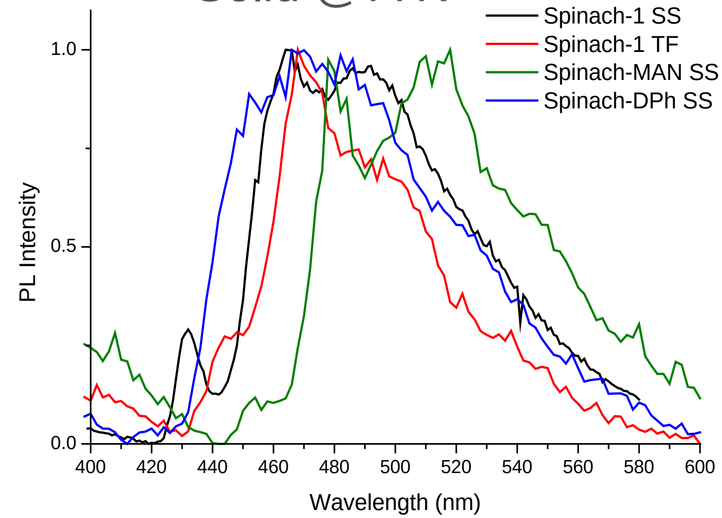
- Very small red shift in the solid state, maintaining high $T_1$ energy.

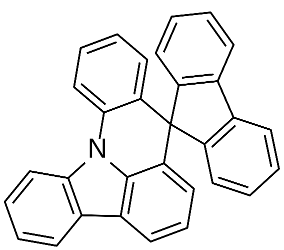
Phosphorescence Spectra

2meTHF @77K

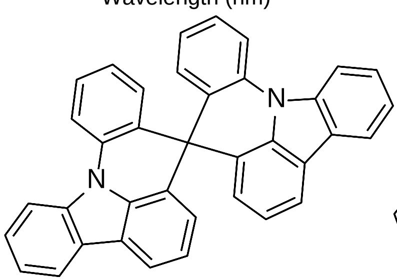



Solid @77K

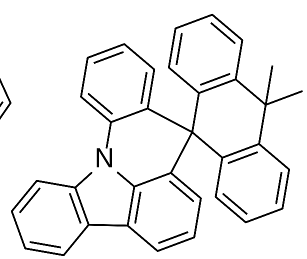


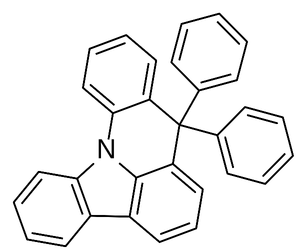

Spinach 1




Spinach 2




Spinach MAN

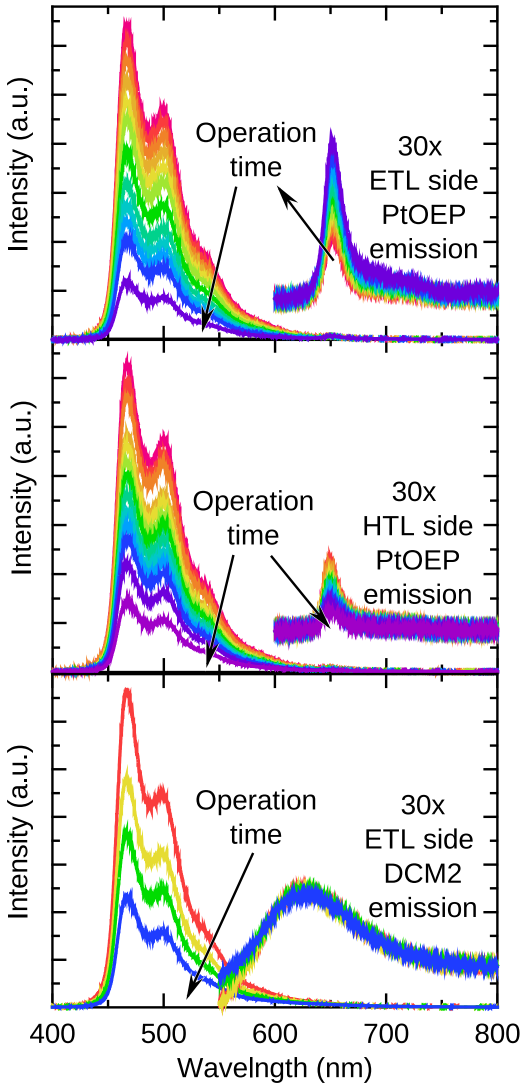


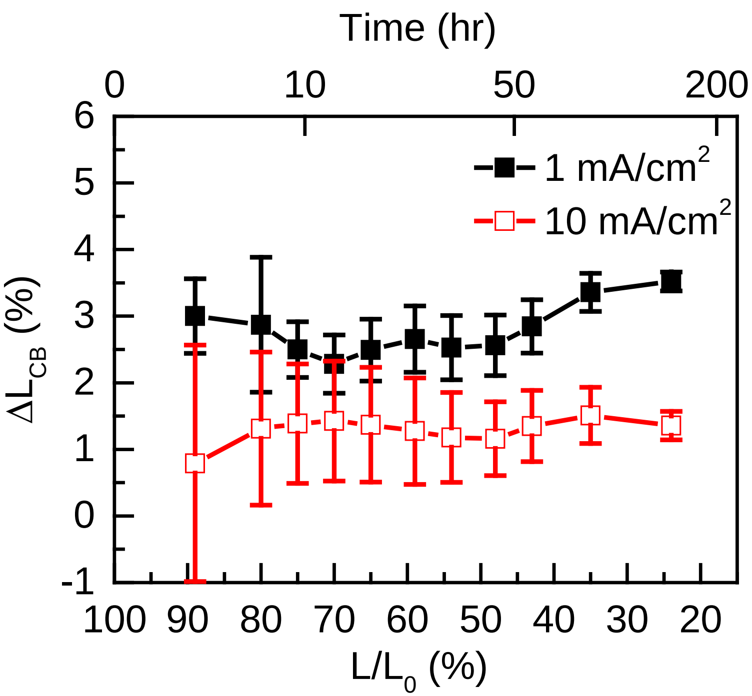

Spinach DPh

PLQY = 0.97 for 5%FIrpic: Spinach DPh

# Progress and Accomplishments (VIII)

Positively determined that increased leakage of charge and excitons not implicated in blue PHOLED degradation.




Charge balance and exciton leakage responsible for <3% of device degradation

Use of sensing layers sensitive means for measuring charge leakage beyond emission zone

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# Impacts

Papers/Patents submitted or presented at international conferences:

1. "Charge balance and exciton confinement in phosphorescent organic light emitting diodes" C. Coburn, J. Lee, and S. R. Forrest, *Adv. Opt. Mater*., **4**, 889 (2016)
2. "Effects of charge balance and exciton confinement on the operational lifetime of blue phosphorescent organic light emitting diodes", C. Coburn and S. R. Forrest, submitted (2016)
3. "Hot excited state management for long-lived blue phosphorescent organic light-emitting diodes", J. Lee, C.Jeong, T. Batagoda, C. Coburn, M. E. Thompson, S. R. Forrest, submitted (2016).
4. "Gram scale synthesis of benzophenanthroline and its blue phosphorescent platinum complex," Patrick J. G. Saris and Mark E. Thompson, *Organic Letters*, in press.
5. "Electrophosphorescent Light Emitting Devices: Challenges ahead for the coming revolution in displays and lighting", S. R. Forrest, *Adavances in Display Workshop*, keynote, Hong Kong (Dec. 16, 2016)
6. "Organic Light Emitting Devices: Challenges Ahead for the Coming Revolution in Displays and Lighting," S. R. Forrest, plenary, *Int. Conf. on Electroluminescence (ICEL 2016)*, Raliegh, NC (Oct. 2-5, 2016)
7. "Blue Phosphorescent OLEDs: Their Prospects in Displays and Lighting ", S. R. Forrest, Y. Zhang, J. Lee, M. E. Thompson, T. Batagoda, H-F. Chen, invited, Paper EP1.1.06, *MRS Spring Mtg.* Phoenix, (March, 2016)
8. "Enhanced emission efficiency for organic LEDs", M. Thompson, W. Brutting, S. R. Forrest, invited, Paper EP1.1.01, *MRS Spring Mtg.* Phoenix, (March, 2016)
9. Organic light emitting diode having a mixed blocking layer, disclosed 9/8/15, U.S. Provisional 62/240,298 filed 10/12/15
10. High-energy excited state manager materials for long-lived blue phosphorescent organic light-emitting diodes, disclosed 10/19/15,U.S. Provisional filed 11/16/15
11. Locally doped excited state manager for long-lived blue PHOLEDs, disclosed 5/16/16, U.S. Provisional filed 5/16/16
12. Triindolotriazine host material to improve OLED performance and lifetime, disclosed 3/12/16, U.S. Provisional to be filed.

**Awards/Recognition**: Thompson and Forrest awarded the Jun-Ichi Nichizawa Medal of the IEEE for development of phosphorescent OLEDs. Forrest elected to the National Academy of Sciences.

**Lessons Learned**: The fragility of the Ir-based manager decreases its utility in extending device lifetime since it is exhausted through use.

# Project Integration and Collaboration

**Project Integration**: Team consists of three organizations: University of Michigan (lead), USC and Universal Display Corp. UM and USC personnel have weekly team telecons to review results and plan future steps. UM and USC meet quarterly at UDC for similar results discussions and planning.

**Partners, Subcontractors, and Collaborators**: University of Michigan: Program lead (Prof. S. Forrest), DOE point of contact. Team of 3 PhD students with tasks in device modeling, fabrication, and lifetime testing. USC (PI: Prof. M. Thompson). Team of 3 PhD students and post-doc with tasks of development of hosts, managers and phosphors. Energetic modeling and library building of potential molecules. UDC: (PI: Dr. M. Hack): Team of 1 PhD to validate lifetime and efficiency data. Build scaled up prototypes.

**Communications**: Several, listed on previous panel. Notably our team has given keynote, plenary and invited talks at several international conferences and workshops.



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# Next Steps and Future Plans

- Continue to gather data on degradation products from operation of blue PHOLEDs to determine weakest bonds. Use this to guide development of new materials
- Continue development of new, high triplet energy hosts
- Continue development of new, high triplet energy managers that are more robust against degradation
- Integrate managers in stacked blue and white PHOLEDs to approach DOE MYPP lifetime goals
- Validate lifetime results at UDC

# REFERENCE SLIDES

# Project Budget

**Project Budget**: The boxed figures are the original budget with actual expenses in the line below.
**Variances**: The program is currently underspent by approximately one calendar quarter.  Data is being collected to evaluate if the project will be completed within the proposed time or if a no-cost time extension should be considered.
**Cost to Date**: 47.7% of the budget has been expended to date
**Additional Funding**: no additional funding required

| Budget History | | | | | |
|---|---|---|---|---|---|
| 9/1/15 – FY 2016 (past) | | FY 2017 (current) | | – 8/31/17 (planned) | |
| DOE | Cost-share | DOE | Cost-share | DOE | Cost-share |
| $659,915 | $203,789 | $163,581 | $57,402 | $490,744 | $172,207 |
| $493,004 | $173,218 | $124,985 | $43,914 | $696,251 | $260,180 |

# Project Plan and Schedule

| Task | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| 1 | | | | G/NG1 | | | | |
| 1.1 | M1.1.1 | | M1.1.2 | M1.1.3 | | | | |
| 1.2 | | | | M1.2.1 | | M1.2.2 | | |
| 1.3 | | | | M1.3.1 | | M1.3.2 | | |
| 2 | | | | G/NG1 | | | | |
| 2.1 | | M2.1.1 | | | M2.1.2 | M2.1.3 | | |
| 2.2 | | | | M2.2.1 | | | M2.2.2 | |
| 2.3 | | | | | | | M2.3.1 | |
| 3 | | | | G/NG1 | | | | |
| 3.1 | | | | M3.1.1 | | | | |
| 3.2 | | | | | | | | M3.2.1 |
| 3.3 | | | | | | | | M3.3.1 |
| 3.4 | | | | | | | | M3.4.1 |

***Go/NoGo Decision Task 1***: Demonstrate a graded *blue* PHOLED (CIE=0.15, 0.31) in single element or stack with an external quantum efficiency >15%, $LT_{70}$ > 3,000 hours at $L_0$=1000 nits

***Go/NoGo Decision Task 2*:** Demonstrate that introducing an excited state sink into a blue PHOLED can extend its lifetime 2X, showing proof of concept.

# Project Plan and Schedule

| Milestone Summary Table | | | | | | |
|---|---|---|---|---|---|---|
| **Recipient: Name:** | The Regents of the University of Michigan, P.I.: Stephen Forrest | | | | | |
| **Project Title:** | Stable, High Efficiency White Electrophosphorescent Organic Light Emitting Devices by Reduced Molecular Dissociation | | | | | |
| Task | Task Title or Subtask Title | Milestone | Mstne # | Milestone Description | Verif. Process | Qtr. |
| 1 | Stable Blue Phosphors and & Hosts Materials | | | | | 1-4 |
| 1.1 | Efficient blue emitting phosphors | M | M1.1.1 | Model **H3** and **H3P** libraries | ID subst. T>2.7 eV | 1 |
| | | M | M1.1.2 | Prep./charac. Ir(**H3**)$_3$ &Ir(**H2P**)$_3$ | ID Ir cmplx >2.7eV,PL>70% | 3 |
| | | M | M1.1.3 | Ir(**H2P**)$_3$ and Ir(**H3**)$_3$ PHOLEDs | Ir phos EQE>12% | 4 |
| 1.2 | High energy electron conducting hosts | M | M1.2.1 | N-substit. **H2P** and **H3** hosts | ID 6 substit. | 4 |
| | | M | M1.2.2 | PHOLEDs w N-substitute hosts | Ir-H2P,H3 EQE>12% | 6 |
| 1.3 | Matched host and dopant materials | M | M1.3.1 | Prep. matched host-dopant | PL>70% | 4 |
| | | M | M1.3.2 | PHOLEDs, match host-dopant | 5000hr/1000cd/m$^2$ | 6 |
| 1.4 | Long-lived Blue PHOLEDs | M | M1.4.1 | Optimal dopant gradient for | 50Khr/1000cd/m$^2$ | 8 |
| 1 | | G/NG | G/NG 1 | Blue PHOLED: eff. > 15%, $LT_{70}$ > 3,000 hr at $L_0 = 1000$ cd/m$^2$ | UM/UDC life test | 4 |
| 2 | Excited State Sinking to Enhance Lifetime | | | | | |
| 2.1 | Development of excited state sinks | M | M2.1.1 | Photostab. of mCBP$^-$ & | Stable polaron tst | 2 |
| | | M | M2.1.2 | Photostab. **H3**,**H2P**, Ir(C^N)$_3$ | ID decomp. prod. | 5 |
| | | M | M2.1.3 | Redux Power **H3**,**H2P**, Ir(C^N)$_3$ | ID 3 sink molec. | 6 |
| 2.2 | Employing excited state sinks blue PHOLEDs | M | M2.2.1 | mCBP-Ir(dmp)$_3$-sink PHOLEDs | EQE=12%,5Khr | 4 |
| | | M | M2.2.2 | host-dopant-sink blue PHOLEDs | 25Khr/1000cd/m$^2$ | 7 |
| 2.3 | Materials and device characterization | M | M2.3.1 | Materials characterization | ID TPQ v TTQ prod | 7 |
| 2 | | G/NG | G/NG 2 | Blue PHOLED: 2X lifetime by excited state sink | UM/USC life test | 4 |
| 3 | Lifetime validation and scaling | | | | | |
| 3.1 | Std character. Of blue and white PHOLEDs | M | M3.1.1 | Validate 1cm$^2$ blue lifetime | 5000hr/1000cd/m$^2$ | 4 |
| 3.2 | WSOLED lifetime characterization | M | M3.2.1 | Validate 1cm$^2$ WSOLED lifetime | 50Khr/3000cd/m$^2$ | 8 |
| 3.3 | WSOLED panel fabrication and validation | M | M3.3.1 | Fab and char (15cm)$^2$ panel | Full lighting char. | 8 |
| 3.4 | Materials and device characterization | M | M3.4.1 | Materials character. post mortem | Opt. designs w rslt | 8 |