Award Number DE-EE0003296 Final Report
Performing Organization University of Rochester
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Title Development and Utilization of Host Materials for White Phosphorescent Organic Light-Emitting Diodes
Reporting Period – February 1, 2010 – May 31, 2013

I. Executive summary

Our project was primarily focused on the MYPP 2015 goal for white phosphorescent organic devices (PhOLEDs or phosphorescent organic light-emitting diodes) for solid-state lighting with long lifetimes and high efficiencies. Our central activity was to synthesize and evaluate a new class of host materials for blue phosphors in the PhOLEDs, known to be a weak link in the device operating lifetime. The work was a collaborative effort between three groups, one primarily responsible for chemical design and characterization (Chen), one primarily responsible for device development (Tang) and one primarily responsible for mechanistic studies and degradation analysis (Rothberg). The host materials were designed with a novel architecture that chemically links groups with good ability to move electrons with those having good ability to move "holes" (positive charges), the main premise being that we could suppress the instability associated with physical separation and crystallization of the electron conducting and hole conducting materials that might cause the devices to fail. We found that these materials do prevent crystallization and that this will increase device lifetimes but that efficiencies were reduced substantially due to interactions between the materials creating new low energy "charge transfer" states that are non-luminescent. Therefore, while our proposed strategy could in principle improve device lifetimes, we were unable to find a materials combination where the efficiency was not substantially compromised.

In the course of our project, we made several important contributions that are peripherally related to the main project goal. First, we were able to prepare the proposed new family of materials and develop synthetic routes to make them efficiently. These types of materials that can transport both electrons and holes may yet have important roles to play in organic device technology. Second we developed an important new method for controlling the deposition profile of material so that arbitrary concentration gradients can be implemented in layers with mixed composition. These concentration profiles are known to increase device efficiency and longevity and we confirmed that experimentally. Third, we investigated a new method for analyzing degradation in devices using mass spectrometry to look for degradation products. We showed that these methods are not simple to interpret unambiguously and need to be used with caution.

II. Comparison of accomplishments with objectives

Our objectives can be summarized by the milestones Table from the original proposal and we can compare our achievements with these on a one by one basis.

Our Table of milestones and success criteria from the original proposal is as follows:

Milestone	Month	Description of activities*	Success criteria
1	3	Host materials sets with characterization	Documented materials
2	6	Exciplex-free host materials	Documented exciplex yields
3	6	Balanced mobility host materials	Documented mobilities
4	9	Balanced mobility and exciplex free host materials	Documented mobilities and exciplex yields
5	10	Scale up synthesis of promising materials	Adequate materials for device fabrication (> 5g)
6	10	Accelerated lifetime testing procedures and testbed	Apparatus and documented procedures in place
7	12	Blue PhOLED ~ 100% IQE using new host materials	Blue PhOLEDs > 90% IQE
8	15	Production of degraded blue devices	Transfer devices to Rothberg lab for analysis
9	15	Evaluation of LC-MS and SERS for degradation	Sensitive to dismantled device materials at 1% level
10	18	Blue PhOLED using graded recombination region	Operating lifetime more than double control devices
11	21	Blue PhOLED with lifetime to 50% > 10,000 hours	95 % IQE, > 10,000 hrs
12	24	Analysis of deliberately degraded blue PhOLEDs	Identify limiting materials and likely degradation processes
13	27	Optimized white PhOLED structure	Performance in MYPP target range
14	30	White PhOLED with > 30 lm/W and suitable color (no extraction enhancement)	Documentation of color and efficiency
15	36	White PhOLED > 30 lm/W, lifetime > 10,000 hours (no extraction enhancement)	Documentation of color, efficiency, longevity
Notes:		* Many of the activities, including device fabrication, are ongoing. Milestone refers to first completion of task.	

Milestone 1 was accomplished for the triazine-carbazole system in June 2011 and is now complete for the second and third materials sets UGH-3/mCP and TPA/TRZ. Milestone 5 on scaleup has been completed for our UGH-3/mCP linked material and we are done for the TPA/TRZ systems as well. We have good data for Milestones 2-4 on the photophysics and charge transport in the linked hosts (and FIrpic doped linked hosts) and the story that is emerging is that the linked hosts have excellent morphological stability and adequate bipolar charge transport but we have not yet found a combination that is not plagued by exciplex formation. Our quantum yield measurements indicate that FIrpic has essentially 100% phosphorescence yield in a TCTA matrix and we need to repeat these in the linked materials to quantify the charge transfer complex issue. Our device degradation testbed (Milestone 6) is operational and we have now produced copious degradation data and devices for analysis (Milestone 8). The MALDI work (Milestone 9) is productive and we will report more in our final report. The compositionally graded recombination region work has gone extremely well and is complete (Milestone 10). These have generated good results that we expect to be prescriptive. It is disappointing but we are nowhere near meeting Milestone 11 which promises long-lived, efficient blue PhOLEDs. Studies on device lifetimes with linked hosts are still under way so we can test the hypothesis that the morphological stability they confer will substantially increase PhOLED lifetimes. We have greatly improved the stability of our electron transport/triplet blocking material (Milestone 12) at the cost of some efficiency and gained some understanding of weak links in the device structure. At present, we have purchased another commercial phosphor and are collaborating to get better phosphors that may help us to extend the device lifetime substantially. At present, we do not believe we are limited by the phosphor. We have developed considerable white device data but so far we have good color (Milestone) but efficiencies only ~ 50% of our target for Milestone 14. We have begun work on white device lifetimes and plan to continue it beyond the time horizon of the proposed work but have not yet reached conclusions from that work.

Stepping back and taking a larger view of our project, we have developed and characterized new materials, achieved a great deal of understanding as to how well these work and why, and invented new ways to deposit layers with better spatial control over mixtures. Having said that, we failed to achieve our “bottom line” objectives as exemplified by milestones 11 and 15 under which we would have produced prototypes suitable for commercialization of white light PhOLEDs.

III. Summary of project activities

This final report will be a detailed review of progress on milestones in the Table. For the purposes of discussion and presenting documentation, it is convenient to divide these into materials development (section A, milestones 1 and 5), device-relevant material characterization (section B, milestones 2-4), material and device degradation analysis (section C, milestones 6,8,9,12) and device development (section D, milestones 7, 10, 11, 13-15).

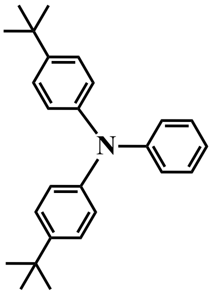
A. Materials development (Design of linked hosts and scale up: milestones 1,5)

It is useful to reiterate the rationale behind our strategy to develop hosts with covalently linked hole transport moieties (HTM) and electron transport moieties (ETM). Mixing HTM and ETM has the effect of stretching out the recombination region which in turn has been shown to increase device lifetime and efficiency. Lifetime is increased because a larger set of dopants can participate in the electroluminescence so that degradation of the phosphor is less problematic. Efficiency is increased because the recombination zone can be move away from interfaces where there can be charge buildup and quenching. However, mixing HTM and ETM molecules is expected to eventually result in phase segregation and we speculated that the attendant mechanical stresses could cause device failure. We hypothesized that the benefits of mixing ETM and HTM could be achieved without the attendant problems associated with phase separation if electron transporting and hole transport chemical units could be covalently linked. To be successful, the linkage would have to occur without corrupting the HOMO level of the HTM and LUMO level of the ETM that are integral to determining the transport properties. Also, the combined entity would have to maintain the high triplet levels in the constituents as required to prevent quenching of the phosphor. Finally, a successful linkage would avoid the potential pitfall of introducing charge transfer states (exciplexes) that could also quench the phosphor. In the present section, we review the materials synthesized and the characterization of their chemical purity. Direct tests of the device relevant properties will be reviewed in the next section.

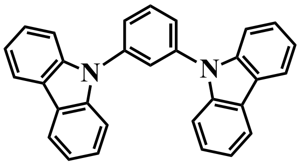
We use the notation the HTM:ETM to denote mixed hosts made through co-evaporation while HTM-L-ETM is used to denote flexibly (alkane) linked hosts. The precise structures of the compounds we synthesized along with synthetic routes, yields, nuclear magnetic resonance and elemental analysis to verify their structure and purity can be found in our annual progress reports. Here, we review what they were and the thinking behind how we chose them. First, it is useful to point out that there is a quite limited set of suitable HTM and ETM with triplet energies high enough to support blue phosphorescent dopants like FIrpic which we used for the bulk of the studies since it is commercially available.

In the first year of the program, we focused on synthesizing linked host systems inspired by the PhOLED literature with HTM based on carbazoles, mCP and $Cz(MP)_2$. Our ETMs were close to phenylsilanes like UGH-3 or triazines (TRZ). In year 2, motivated by success in making 100% internal quantum efficiency blue PhOLEDs based on TCTA:UGH-3 mixtures, we switched to triphenylamine (TPA) HTMs that are very similar structurally to TCTA. This change was also motivated by literature reports that carbazoles such as mCP are generally unstable. To confer better electrochemical stability on the TPA units, we synthesized variations with tBu ligands on the TPA that exhibit much better stability. In our final year, we experimented with changes in the linkages, comparing the relative efficacy of flexible non-conjugated linkages between HTM and ETM with *para*- and *meta*- linkages through rigid aromatic moieties to better understand the role of flexibility in the linker.

For concreteness, some examples are shown in Figure 1 but these are discussed in much more detail in our progress reports. Altogether, we made and fully characterized around a dozen linked host complexes in high yield and purity on scales large enough to fabricate and test PhOLEDs. We provide an overview of the materials properties achieved in section B and their use in devices in section C. It is important to note that our original success metric was to fabricate 5 grams of each material to be tested, our original estimate of the amount needed for subliming many times to make optimized PhOLED structures. One achievement of the program was the development of deposition boats with side hole monitors that could be packed tightly and held close to the device substrate thereby reducing material usage by an order of magnitude. We were therefore able to make optimized PhOLEDs with as little as 200 mg of various linked complexes.



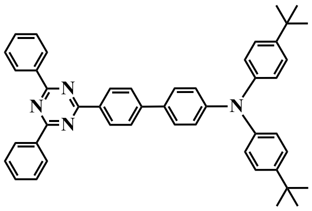
***t*Bu-TPA**



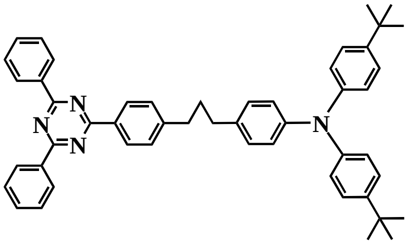
TRZ

E_{T} of **TPA**: 3.07 eV (expt’l)
Russian Chemical Bulletin **2008**, *57*, 257-262

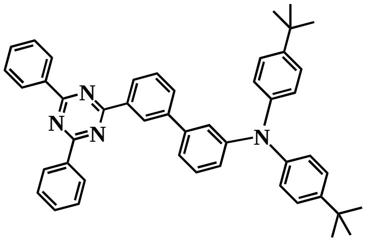
E_{T}: 3.03 eV (expt’l)
J. Mater. Chem. **2009**, *19*, 8772-8781



***t*Bu-TPA-*p*-TRZ**



***t*Bu-TPA-ℒ-TRZ**



***t*Bu-TPA-*m*-TRZ**

Figure 1: Linked triphenylamine and triazine structures.

B. Device relevant materials characterization (milestones 2-4)

In the present section, we assess whether we have imbued the materials synthesized with the targeted properties. In particular, we evaluate (1) whether we have successfully imported the HOMO and LUMO of the constituent HTL and ETL respectively with electrochemical and transport measurements, (2) whether we have maintained high triplet energy with low temperature luminescence measurements of the linked complexes designed to look at phosphorescence. (3) whether we have suppressed excimer formation by comparing absorption and photoluminescence to those of the separated HTM and ETM and (4) whether we have indeed suppressed crystallization by using differential scanning calorimetry (DSC) and polarized optical microscopy (POM).

Energy levels and charge transport: In every case of the linked complexes that, electrochemical measurements showed that our strategy successfully leaves the HTM and ETM decoupled so that the linked complex “imports” the HOMO of the independent HTM and LUMO of the independent ETM. Most of the systems showed reversible reduction and oxidation peaks. Time-of-flight photoconductivity measurements were made on both the mCP-L-SiPh$_3$ family of complexes and the TRZ-Cz(MP)$_2$ family and each had relatively low electron and hole mobilities and dispersive transport. Encouragingly, however, both sets of materials had ambipolar transport measurable by time-of-flight photoconductivity and the mobilities were in the range exhibit by successful OLED hosts. We decided in year 2 to abandon the mobility measurements for several reasons, the primary one being that the time-of-flight in thick films does not necessarily represent what would be observed in a thin OLED film.

Triplet energy: Triplet energies for the linked complexes were measured using low temperature phosphorescence. Those that displayed clear phosphorescence had triplet energies consistent with the energy of the HTM which in all cases had triplet below that of the ETM. Unfortunately, some of these measurements were complicated by the formation of exciplexes that also show red-shifted emission as will be discussed below.

Exciplex formation: In the mCP-PhSiPh$_3$ systems, we saw only triplet emission in low temperature measurements but in the the linked triphenylamine-triazine complexes exciplex formation was observed even in dilute frozen glasses. The exciplex formation was much more prevalent in the para and meta linked complexes than the one with flexible non-conjugated linker but even in the latter there was evidence for exciplexes. In some cases, these charge transfer states were even observed as a small bump on the red end of the absorption spectrum (see Figure 2).

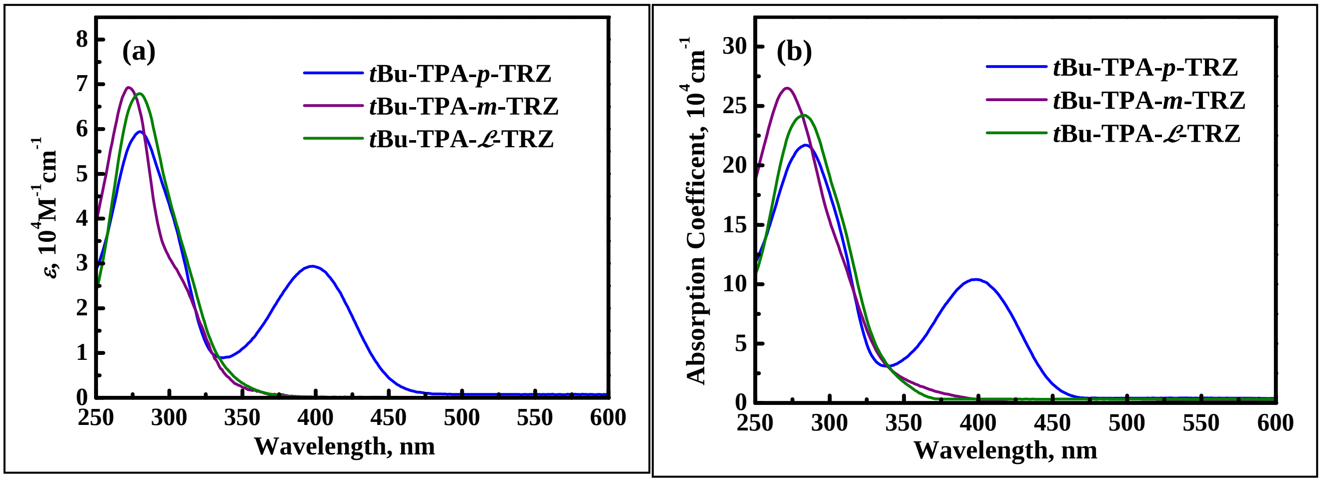


Figure 2. Absorption of linked complexes in ~ 8x10^{-6} M chloroform solution (left) and neat ~ 100nm films (right).

This was a key finding of our work and we ascribe the relatively low efficiency of the blue PhOLEDs based on our linked hosts to the formation of exciplexes that are lower in energy than the phosphor's triplet state. If a molecular design could be found that eliminates that problem, our host strategy could be promising.

Improved morphological stability: Polarized optical microscopy was done to determine whether films of the mixed HTM and ETM and films of the linked HTM and ETM differed in morphology and whether the linakge suppressed phase segregation. In every case, the linked host material failed to crystallize even with severe annealing and its glass transition as measured by DSC was much higher (~ 50 – 100 °C) than that of the mixture. The measurements were made between ITO/glass and aluminum to simulate device conditions. Another key finding of our program is that the improved morphological stability does matter in a real PhOLED and we review our proof in the section C where we compared the degradation of PhOLED devices based on mixtures with those based on linked complexes under thermal stress.

C. Device efficiency results (milestones 7,10,11,13-15)

Milestones 7,10 and 11 that concern blue device efficiency will be reviewed in the first part of the present section followed by milestones 13-15 that pertain to white PhOLED development. With regard to the blue devices, we maintained parallel efforts, one pursuing devices based on the covalently linked hosts and a second based on more traditional mixed hosts. In each case, the primary phosphor used was FIrpic though we investigated others towards the end of the program.

Blue "traditional host" devices: Our initial point of study for the traditional devices was following the work of Lee and coworkers (*Appl. Phys. Lett.* **2008**, *92*, *133304*), a group that demonstrated nearly 100% IQE PhOLEDs using mixtures of TCTA and UGH-3 as host materials. Typical structures and results are shown in Figure 3 where optimal FIrpic doping of the emissive layer was found to be ~ 12%.

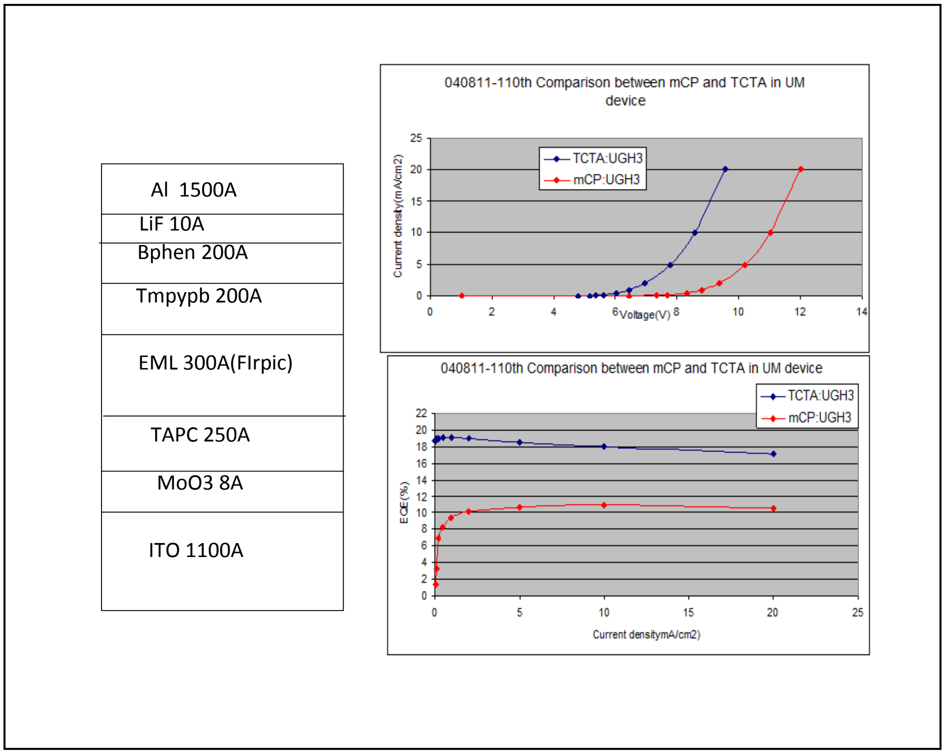


Figure 3. Blue PhOLEDs based on co-evaporated mixed hosts mCP:UGH-3 and TCTA:UGH-3

While these devices satisfied our efficiency milestones, they were exceedingly unstable with half lives of less than an hour and this will be discussed further in section D where we review degradation analysis. We were unable to improve upon this stability without considerable degradation of efficiency.

Graded host layers for blue PhOLEDs: Our invention of low thermal mass deposition boats with side hole monitoring allowed us to implement a feedback system so that we could arbitrarily vary the host concentration profiles through the emissive layer. We did extensive studies of how this affected blue PhOLED properties and the publication resulting from these studies won a Society for Information Display best paper award. Figure 4 shows how linear grading (LGM) of the HTM/ETM concentration profile in the emissive layer compares to uniform mixing (UM). In addition, one can see that the recombination is heavily biased on the electron transport layer side of the device. Moreover, one can see from the data in Figure 4 where we remove dopant that the recombination region is definitely extended in the LGM since it is much less affected by removal of the phosphor near the interface. We believe that the grading will increase lifetime by extending the recombination region but have not tested that.

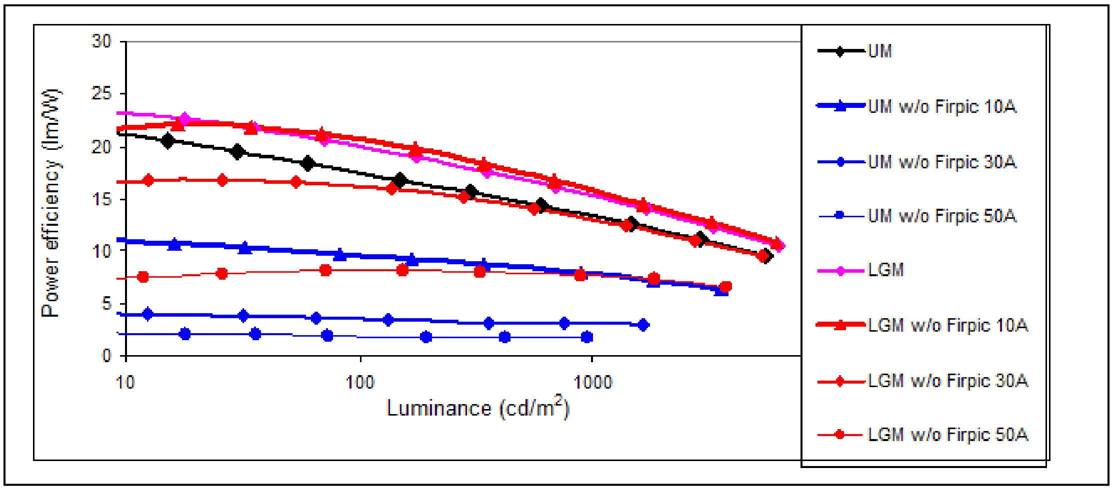


Figure 4. Comparison of efficiency for FIrpic PhOLED devices with linear host grading (LGM) and uniform host mixing (UM) as the FIrpic is removed from the ETL side of the emissive layer.

Linked host blue devices: In year 1, we achieved ~ 100% IQE using TCTA:UGH-3 mixed host layers while observing that we could only reach ~ 50% IQE with the analogous mCP:UGH-3 host. When we found that our mCP-L-$SiPh_3$ family of linked hosts did not perform above ~ 40% IQE, we thought that designing TPA-L-TRZ systems might help since TPA much more closely resembles TCTA. As illustrated in Figure 5, this was not successful. Optimized ITO/MoO_3 (3 nm)/TAPC (30 nm)/*t*Bu-TPA-*L*-TRZ:FIrpic (15%, 20 nm)/TmPyPB (10 nm)/BPhen (30 nm)/LiF (1 nm)/Al (100 nm) devices provided less than 2% EQE. The t-Bu-TPA-L-TRZ device spectrum shows a red tail in the emission relative to the FIrpic spectrum and we believe this reflects the contribution of exciplexes as shown previously in Figure 2(b). Photoluminescence quantum yield measurements on 15% FIrpic doped films in these hosts gave 45% and 6% respectively for mCP-L-$PhSiPh_3$ and t-Bu-TPA-L-TRZ, consistent with the device data. These results strongly suggest that the performance of the TPA-L-TRZ family is spoiled by the presence of exciplexes. This conclusion was confirmed by analogous device studies using the red emissive dopant $Ir(piq)_3$. In that case, relatively efficient devices (EQE 6%) were fabricated with t-Bu-TPA-L-TRZ hosts. The high energy of the $Ir(piq)_3$

HOMO biases recombination to occur on the dopant and reduces the likelihood of forming exciplexes in the host material.

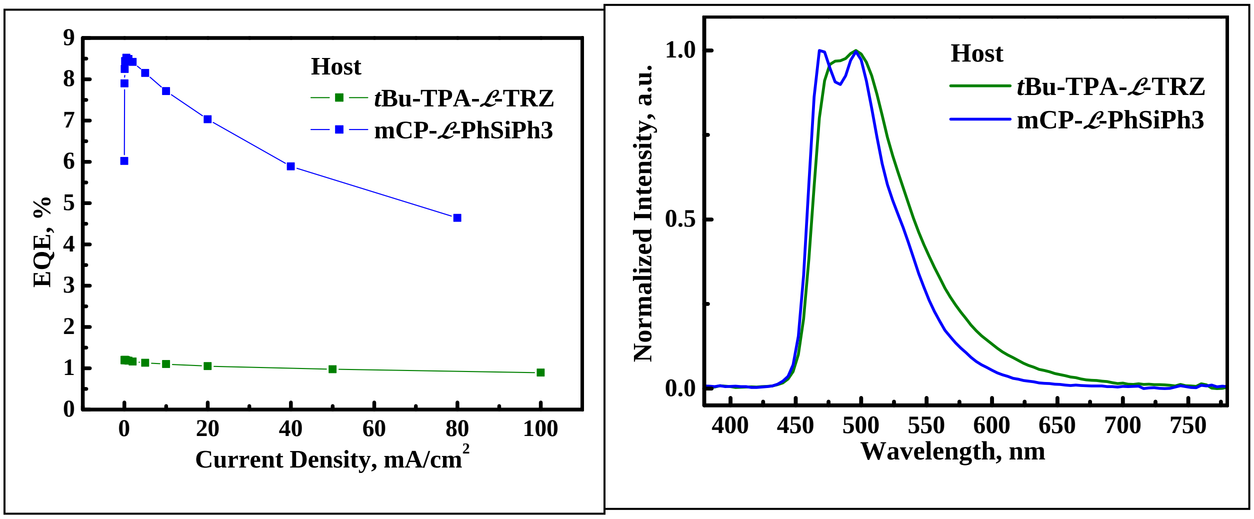


Figure 5. EQE and spectra of FIrpic PhOLEDs based on linked hosts. In each case, the structures are ITO/MoO_3 (3nm)/NPB (30nm)/TAPC (30nm)/Host:FIrpic (10%, 20nm)/ TmPyPB (10nm)/BPhen (30nm)/ LiF(0.8nm)/Al (100nm).

Using the mCP-L-$PhSiPh_3$ host, we were able to obtain up to ~ 50% IQE (similar to what is obtained in mCP:UGH-3, the $PhSiPh_3$ being a close analog of UGH-3). While we were very encouraged by these results, we were disappointed that replacing the mCP with a HTM more like TCTA did not enable us to improve the efficiency. This may have been due to the introduction of TRZ as the ETM (done to reduce synthetic complexity). Nevertheless, we were able to use our linked hosts doped with FIrpic in very important device degradation studies described below that clearly establish the role of morphological contributions to device degradation.

White light PhOLEDs: We have systematically studied two white device architectures (cf. Figure 6) and worked towards optimizing them. When the CIE coordinates are close to 0.33, 0.33, the best devices have drive voltages around 8V, luminance 500 – 2000 cd/m^2, power efficiency of 5 – 10 lm/W, EQE around 8-10% and color that varies ~ 0.01 in CIE x and ~ 0.03 in CIE y with drive voltage. we believe that recombination occurs mostly on the hole transport side of the device (in the Ir(ppy)3 and FIrpic and then triplet migration produces some excited Ir(piq)3 that emits. Our most promising device configuration was MoOx(1 nm)|TAPC (30 nm)|Ir(phq)2acac 6% and Ir(ppy)3 (18%) in mCP|FIrpic 15% in TCTA:TPBi (4 nm)|TmPyPB (10 nm)|BPhen (20 nm)|LiF (1 nm)|Al and it ran at 18.9 lm/W (1600 cd/m^2, 13.4 % EQE) with 5.3 V drive voltage and CIE coordinates of x = 0.3266 and y = 0.4389. Spectra are shown in Figure 7.

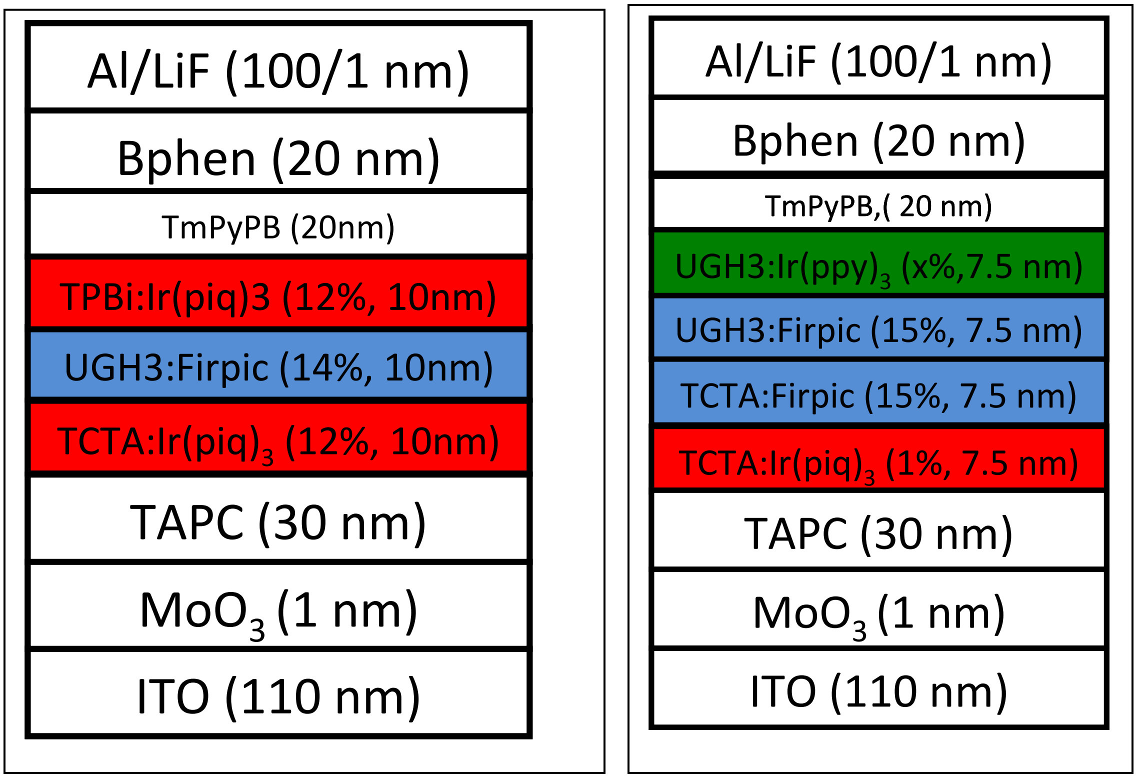


Figure 6. General layer structure of the white PhOLEDs investigated here.

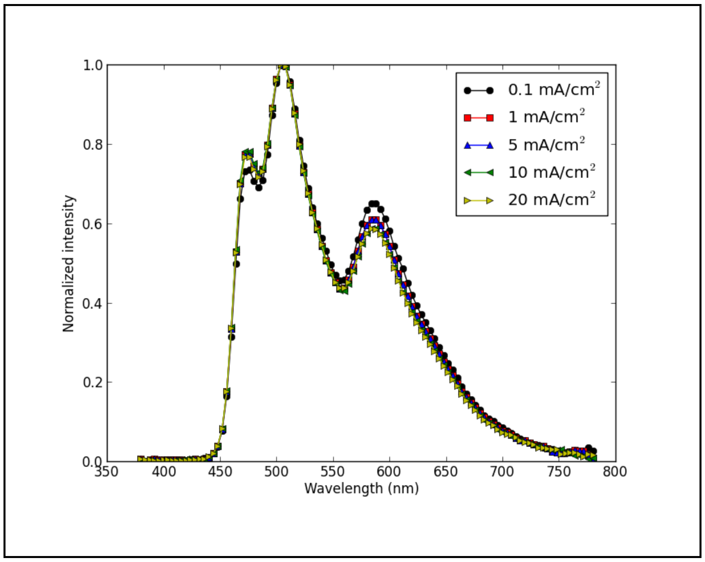


Figure 7. Emission spectrum of 18.9 lm/W white device described in the text.

Some general conclusions we have reached from our white PhOLED studies are as follows. (1) Our ETL and HTL seem to keep the drive voltage above 5 V and limit our power efficiencies (note: we would be close to meeting our white efficiency milestone at 3V). When we try to reduce voltages by doping the transport layers (e.g. doping BPhen with Cs), this has reduced device efficiencies. (2) TmPyPB is crucial to the high quantum efficiency and we have not been able to replace it without significantly lowering the EQE. (3) Using mixed hosts in the blue emitting layer improves the color balance in the devices but at the cost of reducing efficiency relative to using a pure TCTA host.

D. Degradation of devices and device materials (milestones 8,9,12)

In terms of characterizing and understanding device degradation, we have three contributions to report. First, we have done seminal studies showing that morphological degradation due to phase segregation in mixed host systems will reduce PhOLED operating times substantially. We will describe those experiments in some detail below. Second, we have implemented and evaluated time-of-flight mass spectrometry (MALDI) as an analytical method to study PhOLED degradation. We will also detail how we used MALDI to understand problems with the excited state stability of our workhorse phosphor, FIrpic. However, we will also explain why we do not think MALDI is straightforward to interpret and why we would not recommend it as a general purpose tool for degradation analysis. Finally, we will review systematic studies of blue PhOLED degradation by variation of the device architecture (layer compositions and thicknesses) and enumerate our conclusions. Those studies are the focus of Kevin Klubek's thesis work and are ongoing.

Morphological degradation in devices with linked hosts: Mixed hosts have distinct advantages in balancing charge transport in the emissive layer so that the recombination region is spatially extended and moved away from the interface with potential quenching species. Therefore, a critical thing to understand is whether morphological stability is actually an important limitation in implementing mixed host layers such that our linked host strategy might be a substantial improvement. We are very proud of our work addressing this issue. To do so, we compared devices using either mCP-L-PhSiPh$_3$ or mCP:SiPh$_4$ (Figure 13) as emissive layer hosts. The PhOLED design is the one we have used extensively, the layer structure being ITO/MoO3(3nm)/TAPC(30nm)/ Host:FIrpic(30nm) /TmPyPB(10nm)/ Bphen(30m)/LiF(1nm)/Al(100nm).

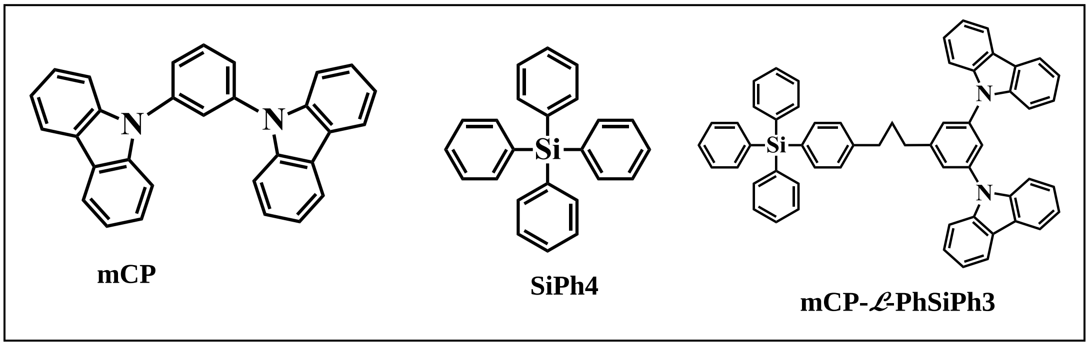


Figure 8: Host materials used to investigate morphology effects on blue PhOLED degradation

We fabricated "half devices" with only the hole transport layer deposited and thermally treat them to verify the morphological and electrical stability of TAPC. Next, we added the host layers with 10% FIrpic doping and compare the stability of the mixed and linked hosts using polarized optical microscopy (in transmission through the transparent anode). Figure 9 presents these data. Crystallization was observed in mCP:SiPh4:FIrpic (10%) films even under mild conditions (20 ºC, 24 hours) but not in mCP-*L*-PhSiPh3:FIrpic (10%) films even under harsh conditions (e.g. 100ºC, 1 hour).

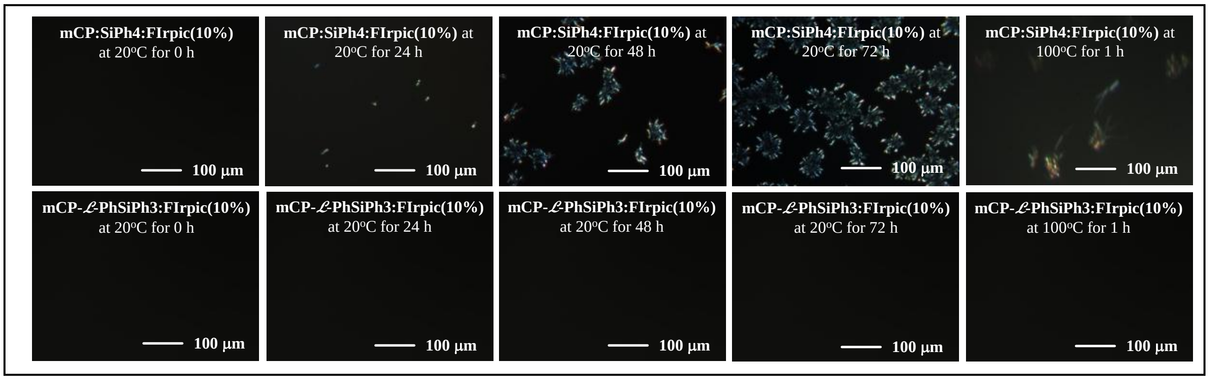


Figure 9. Polarized optical micrographs of mCP:SiPh$_4$ (top) and mCP-L-PhSiPh$_3$ (bottom) under various annealing conditions.

Next we made complete devices with unannealed mixed and linked host layers since it is possible in principle that adding the overlayers would suppress crystallization so that the measurement of Figure 9 would be misleading. We made PhOLEDs where the EML was annealed and the device completed and one where the device was completed prior to annealing and the full device annealed. Remarkably, these gave the same results. The former data are shown in Figure 10 where we compare device performance with the mixed host and linked host after the same annealing conditions were applied to the full devices that we used in Figure 9. The mixed host layer device initially has superior performance but degraded rapidly with annealing while the linked host device is less efficient but is much more robust. We think that these data conclusively show that EML morphological stability does matter to device operating lifetime and that the morphological properties are improved using the linked host strategy.

Microscopic analysis of device degradation: In consultation with DOE, we replaced surface enhanced Raman spectroscopy and liquid chromatography-mass spectrometry (LC-MS) in favor of laser desorption mass spectrometry (“MALDI”) to study the chemical transformations relevant to device degradation. This change in plans was motivated by two factors. First, the MALDI appears to be more sensitive and second, the Leo group has shown (and we confirmed) that it is possible to analyze degradation in complete OLEDs without “deconstructing” them by using the MALDI laser to “drill” through the cathode (Al).

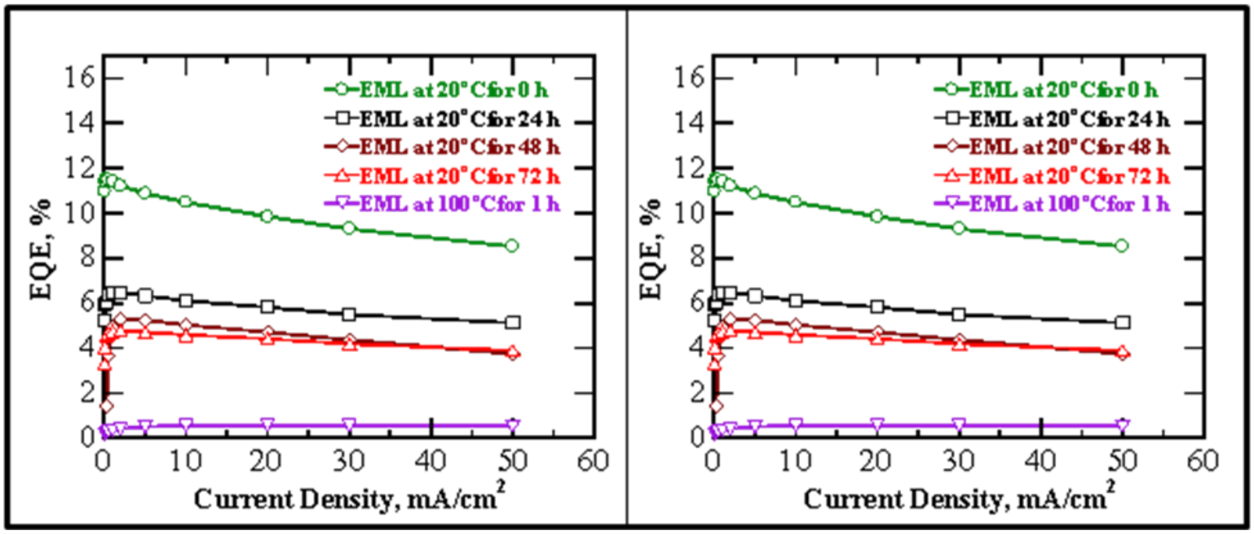


Figure 10. Device efficiency after the stated annealing conditions for PhOLEDs that are nominally identical other than their emissive layer hosts, mCP-L-$PhSiPh_3$ (left) and mCP:$SiPh_4$ (right). Note that in each case, the drive voltages drop significantly when there is annealing, presumably reflecting improved transport as the material becomes more ordered.

After verifying that we could get MALDI spectra from PhOLED devices, we began with simpler experiments on photoexcited degradation of our phosphor, FIrpic. Our thinking was that we could do material by material studies of degradation where we create excited states by optical excitation and electrochemical degradation by analyzing holes-only and electrons-only devices that are analogous to the complete PhOLEDs. We have done the former for FIrpic and the latter for holes only studies of the mixed hosts. The photochemical degradation of FIrpic was reported previously using MALDI by the Leo group who posited two different chemical pathways. However, after extensive study we concluded that only one of these was a valid pathway and the other is an artifact of failing to carefully control the MALDI laser power. The upshot of our studies is that oxygen chemically attacks FIrpic to release a picolinate ligand. We ran a series of experiments was run to determine the source of that oxygen which could potentially be from trace oxygen in the nitrogen environment, from oxygen in the glass/ITO substrate or from atoms in other FIrpic molecules in the film (our UGH-3 host contains no oxygen atoms). This distinction is important since we want to know whether this is an intrinsic problem (ITO from other FIrpic molecules) or soluble in principle (oxygen from the enviorment of ITO). We found using isotopic studies that the oxygen derives from other FIrpic atoms (Figure 11). One conclusion of these experiments is that we should look for other phosphors without oxygen. A second conclusion based on the rate of degradation per absorbed photon (i.e. per created excited state) was that FIrpic cannot be cycled through its excited state enough times to satisfy the 10,000 hour LD50 milestone (#11) in our proposal. For this reason, we began to seek other phosphors as discussed below.

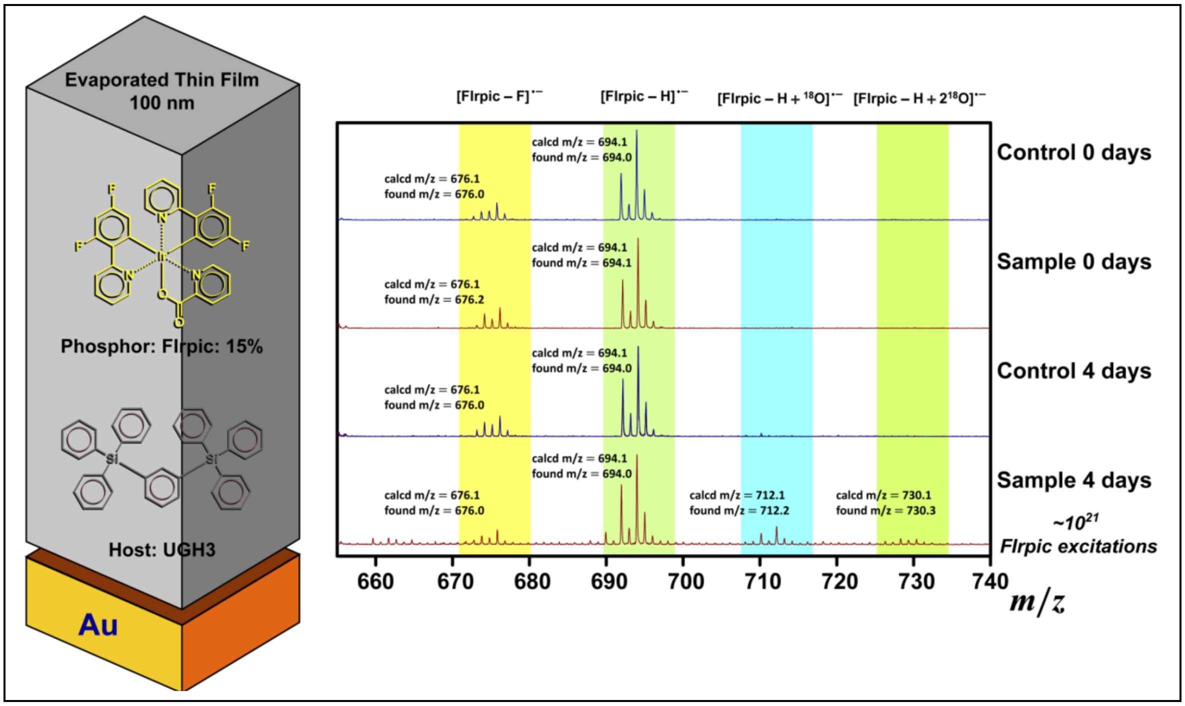


Figure 11. MALDI data on photodegradation of FIrpic in a UGH-3 host.

Device degradation: We designed a testbed to monitor current-voltage and light-emission characteristics during lifetime testing (i.e. deliberate electrical degradation) of various blue PhOLED structures. Since we were able to achieve essentially 100% IQE with devices having layer structure (ITO/MoO_3 (1 nm)/TAPC (30 nm)/TCTA:UGH-3:FIrpic (15%, 30 nm)/TmPyPB (20 nm)/BPhen (20 nm)/LiF (1 nm)/Al (100 nm)), our initial studies used these and we varied layer thicknesses and compositions to better understand which materials and interfaces play an important role in the blue PhOLED degradation. Because we identified the ETL side of the emissive layer as the recombination zone, we looked carefully at the TmPyPB triplet blocking layer on the ETL side of the device since we know that is near the recombination region (see section IIIC). Typical data are shown in Tables 1 and 2. We have dozens of such studies.

The following are amongst the central conclusions from our device degradation studies:

1) TmPyPB is unique in its ability to produce high efficiency devices as a triplet blocker but others appear to be much more stable. Subsequently, we found that moving the recombination interface to the HTL side of the device by introducing hole traps in the emissive layer, enables one to maintain the high efficiency while using TmPyPB and achieving orders of magnitude better stability.
2) NPB quenches triplet excitons and is not a good HTL.
3) Even though we identified oxygen and the picolinate ligand as the weak link in FIrpic, F_2(ppy) which has no oxygen and no picolinate ligand does not greatly improve device longevity. Similarly, model devices using Ir(ppy) and $Ir(piq)_3$ using nominally identical device structures also have poor lifetime.

Remove TmPyPB and systematically vary UGH-3 thickness

ITO|1nm MoO3| 35 nm TAPC| 40 nm EML| UGH3| 500 nm Bphen| LiF|Al

TCTA:Firpic	401	403	400	400	402	402
	87:13	87:13	88:12	88:12	87:13	88:12
UGH3		13	25	50	100	200
Bphen	500	500	500	500	500	500
LiF	10	10	10	10	10	10
Al	1000	1000	1000	1000	1000	1000
Data at 5 mA/cm2	**1**	**2**	**3**	**4**	**5**	**6**
Voltage (V)*	4.6	4.9	5.1	5.4	6.7	8.8
cd/m2	444	733	1007	1274	234	352
cd/A	8.9	14.7	20.1	25.5	4.7	7.0
CIE x	0.161	0.160	0.159	0.159	0.163	0.174
CIE y	0.383	0.383	0.378	0.376	0.384	0.408
Peak (nm)	476.0	475.0	475.0	474.0	497.0	498.0
Bandwidth (nm)	66.2	66.3	66.2	66.9	70.4	74.6
%EQE	**4.0**	**6.6**	**9.2**	**11.7**	**2.1**	**3.0**
t50 @ 5 mA/cm2 (minutes)	**200**	**140**	**35**	**10**	**11**	**120**

Removing TmPyPB improves device lifetimes, UGH-3 may be source of instability

Replacement of UGH-3 with BAlq

ITO|1nm MoO3| 35 nm TAPC| 40 nm EML| BAlq| 500 nm Bphen| LiF|Al

TCTA:Firpic	400	401	403	403	401	401
	87:13	87:13	88:12	87:13	88:12	87:13
BAlq		10	25	50	100	200
Bphen	500	500	500	500	500	500
LiF	10	10	10	10	10	10
Al	900	900	900	900	900	850
Data at 5 mA/cm2	**1**	**2**	**3**	**4**	**5**	**6**
Voltage (V)*	4.6	4.8	4.9	5.1	5.6	6.6
cd/m2	539	600	624	843	844	821
cd/A	10.8	12.0	12.5	16.9	16.9	6.4
CIE x	0.156	0.158	0.162	0.169	0.176	0.198
CIE y	0.376	0.377	0.383	0.397	0.407	0.439
Peak (nm)	476.0	476.0	476.0	487.5	498.0	502.0
Bandwidth (nm)	63.1	64.3	66.2	71.8	74.3	82.0
%EQE	**5.0**	**5.5**	**5.6**	**7.3**	**7.2**	6.5
t50 @ 5 mA/cm2 minutes	**~200**	**300**	**450**	**390**	**350**	**>360**

Using BAlq reduces efficiency (triplet leakage?) but greatly improves lifetime

Program achievements and legacy:

Below we list what we consider to be achievements and important learnings from the project.

- Development of a new class of materials with ambipolar transport that has promise for being good hosts for blue phosphors while having superior morphological stability. In particular, we are able to "import" the high triplet energies and HOMO and LUMO of HTM and ETM constituents.
- Systematic studies showing that morphological stability of the host layer does matter to PhOLED performance and that simply mixed hosts suffer from the propensity to crystallize and phase segregate.
- Construction of new combinatorial coaters with low thermal mass boat design enabling rapid feedback to implement graded host architectures. A linearly graded architecture has been studied extensively using methods to map the recombination region that we have developed.
- Implementation of MALDI for analysis of material and device degradation plus hypothesizing a chemical mechanism for FIrpic degradation that shows how this type of analytical work could be prescriptive under some circumstances.
- Construction of a testbed for OLED operating lifetime studies and initial results identifying specific materials problems in our device architecture. Understanding that the TmPyPB triplet was critical to efficiency and could be greatly stabilized by moving the recombination region to the HTL side.

Program difficulties and remaining challenges:

- Poor efficiency of linked hosts in PhOLEDs leading to best results of 50% IQE. Identification of exciplexes that may reduce efficiency in the current sets of linked host materials.
- Poor device lifetimes that remain far from the stability targets set out in the program milestones.
- Demonstration that MALDI from full devices is not easy to interpret even when full MALDI baseline data from each of the constituent materials is available.
- FIpirc and F2(ppy) are not satisfactory phosphors for meeting the stability requirements. We are still working to obtain others as our studies continue beyond the lifetime of the program and we will continue to report on significant progress.

V. Budget

Our project was on budget. The institutional cost share has been fulfilled and was documented in the financial report from the University.

VI. Publications under DOE support

1) Wang, Q.; Wallace, J.U.; Lee, T.Y.H.; Ou, J.J.; Tsai, Y.T.; Huang, Y.H.; Wu, C.C.; Rothberg, L.J.; Chen, S.H., "Evaluation of propylene-, meta-, and para-linked triazine and tert-butyltriphenylamine as biploar hosts for phosphorescent organic light-emitting diodes", J. Materials Chem. C 1, 2224-2232 (2013). DOI: 10.1039/c3tc00588g

2) Lee, T.Y.H.; Wang, Q.; Wallace, J.U.; Chen, S.H., "Temporal stability of blue phosphorescent organic light-emitting diodes affected by thermal annealing of emitting layers", J. Materials Chem. 22, 23175-23180 (2012). DOI: 10.1039/c2jm35050e

3) Lee, S.M.; Tang, C.W.; Rothberg, L.J., "Effects of emitting layer host composition profile on the recombination zone of blue phosphorescent organic light emitting diodes", J. Soc. Information Display 21, 55-59 (2013). DOI: 10.1002/jsid.141

4) Lee, S.M.; Tang, C.W.; Rothberg, L.J., "Effects of mixed host spatial distribution on the efficiency of blue phosphorescent organic light-emitting diodes", Appl. Phys. Lett. 101, 043303 (2012). DOI: 10.1063/1.4739499

5) Lee, S.M.; Tang, C.W.; Rothberg, L.J., "Improved blue phosphorescent OLEDs with a linearly graded mixed host architecture", Digest of Technical Papers – Society for Information Display International Symposium (2012).

6) Lee, S.M.; Tang, C.W., "Fabrication of a blue organic light-emitting diode with a novel thermal deposition boat", J. Vac. Sci. and Tech. B 29, 062401 (2011). DOI: 10.1116/1.3656392

In preparation:

Lisong Xu and Ching Tang: White light PhOLED studies

Alex Shveyd, Austin He and Lewis Rothberg, MALDI analysis of FIrpic degradation

Kevin Klubek and Ching Tang: Degradation analysis of blue PhOLEDs