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Final Scientific Report
Multifunctional Optical Outcouplers for Efficient and Stable White OLEDs.

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Abstract

Replacing fluorescence by phosphorescence in OLED-based solid-state lighting can realize the Department of Energy's efficiency target of 83% Internal Quantum Efficiency (IQE). The principal challenge, however, is to fix the poor stability of phosphorescent blue OLEDs. To address this, we have fabricated novel plasmonic architectures that improve device stability by decreasing the exciton lifetime of the emitters without drastically decreasing the light extraction efficiency. We describe the impact on stability of these structures in high efficiency blue phosphorescent OLEDs. Although the benefit is appreciable, we find that targeting 'bright' triplets on phosphorescent emitter molecules is an incomplete solution, and that it is also necessary to stabilize 'dark' triplets formed in the host and blocking layers. We demonstrate substantial improvements in stability using the latter approach, and conclude with a discussion of potential approaches to managing dark triplets in OLEDs.

Detailed Description

Organic light emitting devices (OLEDs) are a promising technology for solid-state lighting. Given their compatibility with non-planar and flexible substrates, and their significantly lower cost per area than conventional inorganic LEDs, OLEDs are especially appropriate as diffuse light sources in large-area and novel architectural fixtures. The adoption of OLED lighting, however, has been impeded by low efficiency in the blue portion of the visible spectrum. Commercial blue OLEDs typically exhibit internal quantum efficiencies of 20-40%, corresponding to only 2-4 blue photons per 10 electrons injected into the device. This loss can be remedied through the use of phosphorescent emission[1], similar to the approach used in commercial green and red OLEDs, where internal efficiencies routinely approach unity.

Unfortunately, high-efficiency blue phosphorescent OLEDs are unstable. Like all OLEDs, blue phosphorescent devices are designed to generate molecular excited states, also known as excitons, from injected electrical charge. But blue excitons contain more energy than green or red excited states, and this excess can contribute to breaking chemical bonds. In addition, it is also possible for excitons to interact with other species, such as a charged molecule or a second exciton[2]. Indeed, the combination of two excitons in a blue OLED will generate a hot state with energy ~ 6eV.

The development of commercial high-efficiency blue OLEDs requires a foundation of chemically stable emissive and charge transport molecules. But the device structure controls the other key determinant of OLED stability - the internal energy density. Typically, it is desirable to spread out the excitons and injected charge within a thick emissive layer, thereby reducing the probability of exciton interactions with charge and other excitons[3].

The internal energy density is related to another device parameter – the 'charge balance'. OLEDs form excitons by forcing the recombination of electrons and holes. Rather than describing a precise mechanism of OLED degradation, 'charge balance' concerns refer to the potential consequences of imperfections in the distributions of electrons and holes. As shown in Fig. 1, charge balance is engineered within the emissive region of the OLED by sandwiching it between blocking layers that confine charge and excitons within the emissive layer. A pile-up of one charge carrier within the emissive layer can lead to a high local density of excitons, thereby exacerbating exciton-exciton and exciton-charge interactions.

The overall energy density and local hotspots caused by poor charge balance can be minimized by rapidly converting excitons into photons[4]. Technologically, the challenge is that the emissive state in high efficiency OLEDs is a spin-1 ‘triplet’ exciton. Triplets are naturally dark states, with spin-disallowed emission. Two approaches have been developed to harness this energy. Phosphorescent OLEDs use heavy metals such as Pt or Ir to mix the spin states[5], allowing light emission. Alternatively, thermally-activated delayed fluorescence (TADF) molecules possess spin states that are very close in energy, again allowing light emission, this time via thermal excitation from the dark state back to a bright state[6]. In this study, we concentrate on phosphorescence because it is also the commercial technology in green and red.

Because phosphorescent OLEDs are designed to maximize their performance by funneling energy to the emissive molecules, stability theories have focused on triplets residing on phosphorescent dyes[4]. In this work, we study the impact of the triplet density in state-of-the-art blue phosphorescent OLEDs. We find that the stability of state-of-the-art blue phosphorescent OLEDs is also dependent on ‘dark’ triplet excitons trapped in the host and blocking layers; see Fig. 1. Although difficult to observe and potentially rare, ‘dark’ triplets are expected to exhibit long lifetimes, which can exacerbate instability.

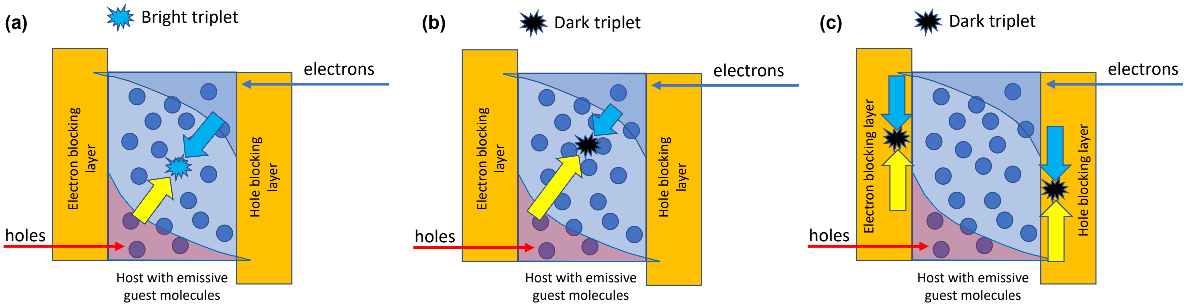

Fig. 1. Electron-hole recombination in an OLED is confined to an emissive region by blocking layers on either side. Here, we consider three different results from electron-hole recombination to form a triplet exciton. The desirable goal is shown in **(a)**, where a triplet exciton is either formed directly on an emissive molecule, or finds its way to the emissive site. In this case, the triplet can emit light and is known as ‘bright triplet’. In **(b)**, the triplet exciton is trapped on a non-emissive host molecule. It cannot emit light and is consequently ‘dark’. Similarly, in **(c)**, triplet excitons are formed in either of the two blocking layers, where they are also ‘dark’.

The impact of bright triplets on OLED stability and droop

We first review the theoretical impact of the triplet lifetime on efficiency droop and device stability. The conventional model of triplet dynamics is:[4]

$$\frac{d[T]}{dt} = -k_R[T] - k_{NR}[T] - \gamma_{TP}[T][P] - \gamma_{TT}[T]^2 + G \qquad (1)$$

Here, $[T]$ is the density of triplet excitons, $[P]$ is the density of charges (described here as polarons to also acknowledge their local polarization distortion field), k_R is the radiative rate, k_{NR} is the non-radiative rate, γ_{TP} is the triplet-polaron interaction constant, γ_{TT} is the triplet-triplet interaction constant, and G is the generation rate of triplet excitons. Note that the radiative rate is non-zero in this model, and consequently these triplets are considered ‘bright’.

In the above equation, the $\gamma_{TP}[P]$ term is dependent on current density. Experimentally, it must be held constant in order to study this system under conditions of constant charge balance. This can be achieved by measuring the efficiency as a function of exciton lifetime at constant current.

Solving Eq. (1) for the quantum yield, η, gives:

$$\eta = \frac{k_R}{k_R + k_{NR} + \gamma_{TP}[P] + \gamma_{TT}[T]}$$

Next, we define the efficiency droop, $\eta_{droop} = 1 - \eta_0/\eta$, where η_0 is the limiting quantum yield at low current densities. This gives:

$$\eta_{droop} = -\tau(\gamma_{TP}[P] + \gamma_{TT}[T]),$$

where τ is the transient lifetime of the bright triplet measured in the absence of electrical bias. Under conditions of constant current density, we expect constant $[P]$, and $[T] \sim \tau$. Thus, if we experimentally vary the Purcell factor, we expect a plot of η_{droop} versus the Purcell Factor to exhibit a slope of between -1 and -2, depending on relative impact on droop of triplet-charge or triplet-triplet annihilation.

Finally, to summarize expectations for OLED stability, we note that triplet-triplet annihilation and triplet-charge annihilation processes are expected to scale quadratically and linearly, respectively, with the density of triplet excitons, $[T]$. Since a resulting defect can quench triplet excitons, the overall luminescence loss is expected[4] to scale like $[T]^n$, where the exponent n=2-3. Indeed, similar power laws (n=2.5-3.5) have been observed in optical studies of phosphorescent dyes[4].

Experimental impact of bright triplets on OLED stability and droop

To compare the theory to experimental studies of OLEDs, it is crucial to study triplets under constant charge balance conditions, which could otherwise influence exciton formation and charge quenching. Consequently, we modulate the density of bright triplets on a phosphorescent emitter by engineering plasmonic coupling to the OLED's cathode. The devices are based on a state-of-the-art blue Pt(II)-tetradendrate emitter, PtON-TBBI[7]. Devices were fabricated on a 100 nm ITO anode with the following device structure: 10 nm HAT-CN hole-injection layer / 100 nm NPD hole transport layer / 5 nm SiBCz electron-blocking layer / 10nm PtON-TBBI doped at 10% into SiBCz as the emitting layer (EML) / 5 nm Si_2TRZPh hole-blocking layer, 15nm BPytP:Liq (50:50) electron transport layer / 2 nm Liq and 1 nm Al electron-injection layers / cathode. The EML is positioned relatively close to the cathode to maximize the effect of plasmonic engineering in the cathode. This approach does not require any structural or chemical modifications within the device and a 1-nm-thick Al charge injection layer was maintained in all devices, to minimize changes in the overall electrical characteristics.

We simulated three cathode variations using the Dyadic Green's Function theory developed by Chance, Prock, and Silbey[8,9]. The predicted modulation of the transient triplet exciton lifetime is characterized by the predicted Purcell Factor, which measures the overall speed up in the combined radiative and non-radiative rates. In particular, as shown in Fig. 2a, we first simulate a 10-nm-thick Ag cathode. It exhibits the largest predicted Purcell enhancement, and is referred to hereafter as the "fast" device. A 10-nm-thick Ag layer with an added stack of 7.5nm of NPD and

5nm of Al, is the “medium” speed device variation, and a conventional 80-nm-thick layer of Al is referred to as the “slow” device. Figure 2b shows simulated Purcell enhancements against wavelength for the three cathode variations for the device stack shown in Fig. 2a. The EL spectrum of the fabricated device structures is overlaid on the Purcell Factor predictions. Integrating over the emission spectrum yields expected speed up factors of 3.1, 2.3, and 1.3 for the fast, medium, and slow devices, respectively. Relative to the slow device, the expected speed up is 2.4× and 1.7× for the fast and medium devices, respectively.

Transient measurements of photoluminescence shown in Fig. 2c were obtained by time-correlated single photon counting. After exclusion of prompt fluorescence from the non-phosphorescent materials in each OLED, a mono-exponential phosphorescent decay is observed for all three device variations with 770 ns, 990 ns, and 1670 ns exciton lifetimes for the fast, medium, and slow devices, respectively. The relative speed up is consistent with predictions: 2.2× and 1.3× for the fast and medium devices with respect to the slow device.

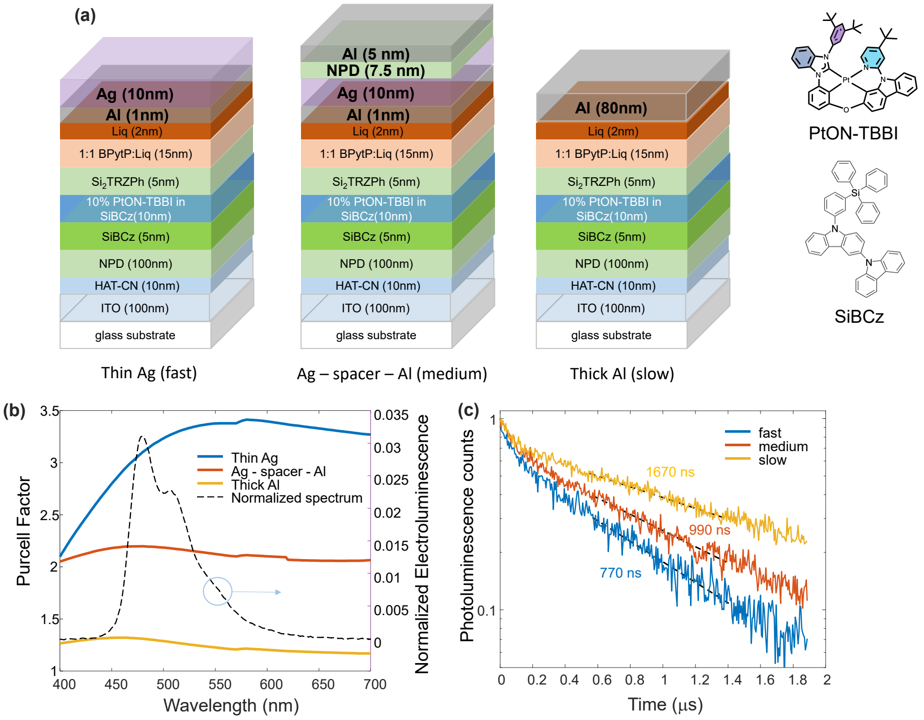

Fig. 2. (a) The device structures of three OLEDs with cathodes engineered for varying plasmonic coupling to the emissive layer. **(b)** Expectations for the Purcell Factor in each of the devices. **(c)** Transient measurements of photoluminescence from each device. Materials are from Ref. [10]. Experiments performed in collaboration with the Jian Li group at ASU.

We fabricated the three devices shown in Fig. 2 and characterize their performance in Fig. 3. The current-voltage characteristics are shown in Fig. 3a, exhibiting nearly identical electronic properties above turn-on voltage. The peak external quantum efficiencies (EQE) of the devices are below 5% showing efficient plasmonic coupling of the emitter induced by the proximity to the cathode. This coupling strength is required to obtain sufficiently large differences in exciton lifetime upon variation of the plasmonic properties of the cathode. The nearly 2× larger EQE of the thick Al-cathode device is due to both the lower plasmonic coupling strength to the EML as well as reflections off the opaque cathode, as device emission is collected through the bottom ITO electrode.

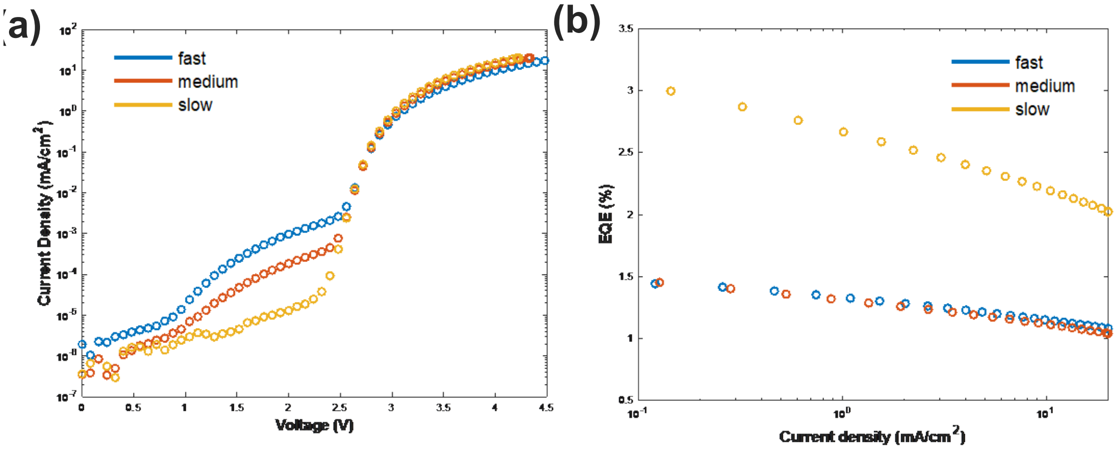

Fig. 3. (a) The current-voltage characteristics of the three devices shown in Fig. 2a. (b) The external quantum efficiency (EQE) of the same three devices as measured through the glass substrate. The efficiency of the 'slow' device is notably higher because of the high reflectivity of the thick Al cathode relative to the semi-transparent 'fast' and 'medium' cathodes. Experiments performed in collaboration with the Jian Li group at ASU.

When we analyze the EQE data in Fig. 4, we find that the dependence of droop on Purcell factor exhibits a power law of 0.43, much weaker than expected under assumptions of either TT annihilation or triplet-charge quenching. This result is consistent with prior studies by Giebink and Forrest[11], in which a similar inconsistency was observed between droop and the transient lifetime of the bright triplets.

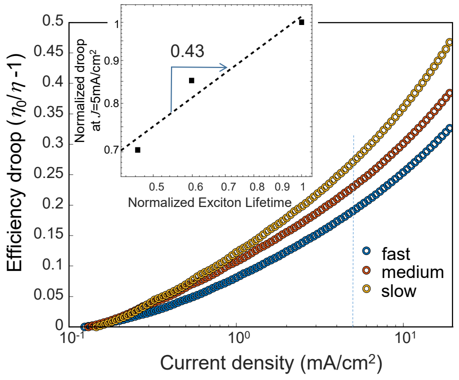

Fig. 4. Analysis of droop as a function of the transient lifetime of bright triplet excitons. Experiments performed in collaboration with the Jian Li group at ASU.

Next, we analyze the dependence of device stability on the Purcell factor; see Fig. 5. Recall that optical studies and theory suggest that the power law dependence of device lifetime on the Purcell factor should exhibit a power law dependence with a slope >2. But the measured slope is -0.55. Again, we observe a much smaller dependence on the lifetime of the bright triplets. Indeed, decreasing the exciton lifetime by a factor of 2.2 yielded an only 1.6× improvement in stability, compared to the improvement by up to a factor of 10 expected from prior optical studies[4].

To confirm the importance of charge carrier balance, we repeat the stability measurement, but this time, we vary the Purcell factor by shifting the position of the emissive zone[12] while keeping the cathode the same, as shown in Fig. 6. We consider four different EML positions, varying the ETL between 15-nm-thick and 30-nm-thick, as schematically shown in Fig. 6a. Moving the EML away from the cathode induces two effects: (i) The exciton lifetime increases due to reduced plasmonic coupling. (ii) The charge carrier balance shifts. Extracting LT90's from EL stability measurements, as described above, yields a power law exponent of 1.55 when comparing device stability and exciton lifetime on a log-log scale. The approximately 3× larger power law compared to the measurement without the confounding effect of varying charge balance shows that charge carrier balance has a more important effect on the stability of these devices than the lifetime of the bright triplet excitons. This confirms that the effect of the bright triplets cannot be isolated if the electrical properties of the device are also varied[12].

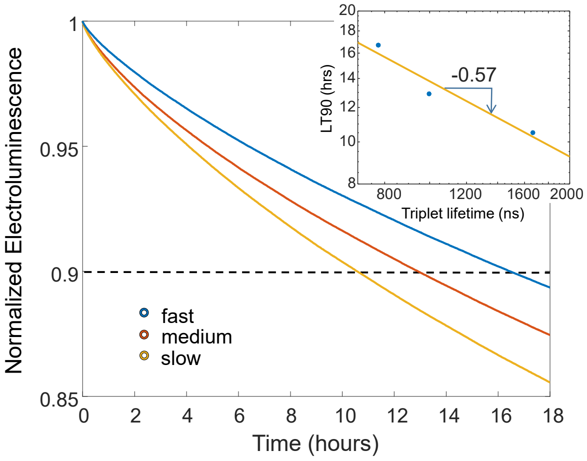

Fig. 5. Stability characteristics as a function of the transient lifetime of bright triplet excitons. Experiments performed in collaboration with the Jian Li group at ASU.

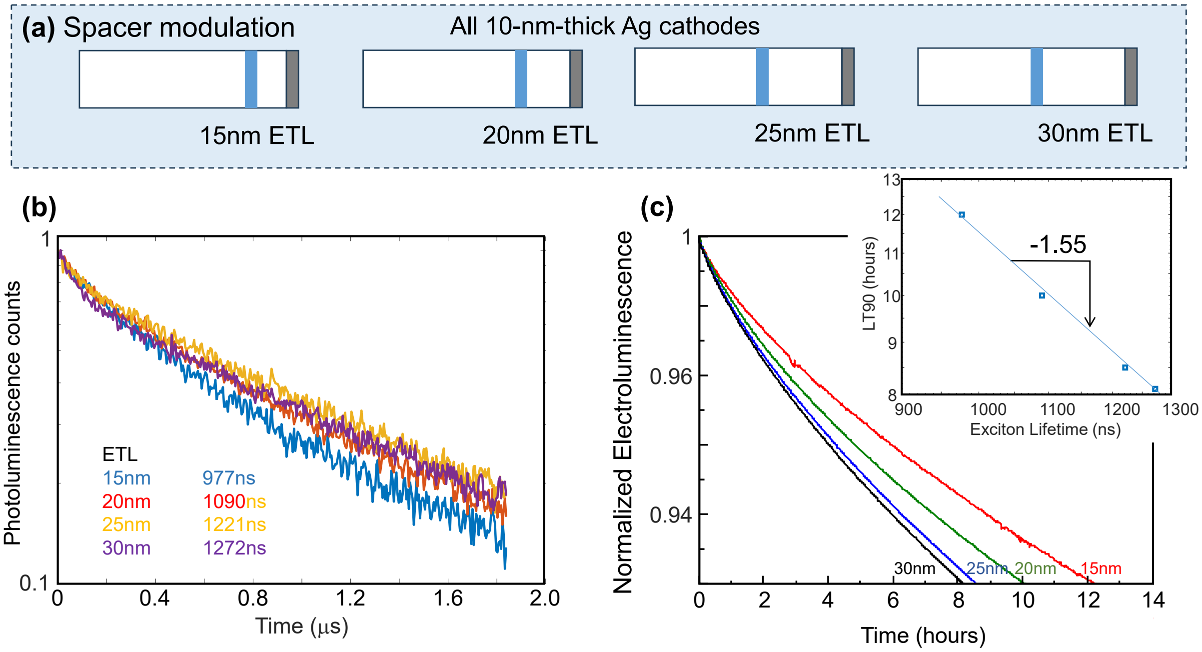

Fig. 6. (a) A schematic representation of a systematic variation in the position of the emission zone within an OLED. **(b)** Transient measurements of the exciton lifetime at different positions within the OLED. **(c)** The corresponding stability data. A comparison of LT90 as a function of the bright triplet lifetime reveals a power law with significantly greater slope than the measurement in Fig. 5, demonstrating the confounding effect of changes in the recombination zone position. Experiments performed in collaboration with the Jian Li group at ASU.

Dark triplets

The results above demonstrate that droop and stability in these blue phosphorescent OLEDs scale as $[T_{br}]^{\sim 0.5}$, where $[T_{br}]$ is the density of bright triplets coupled to the cathode. The dependence on $[T_{br}]$ is much weaker than expected from theory or observed in prior photoluminescence studies, and it cannot be explained by varying charge balance.

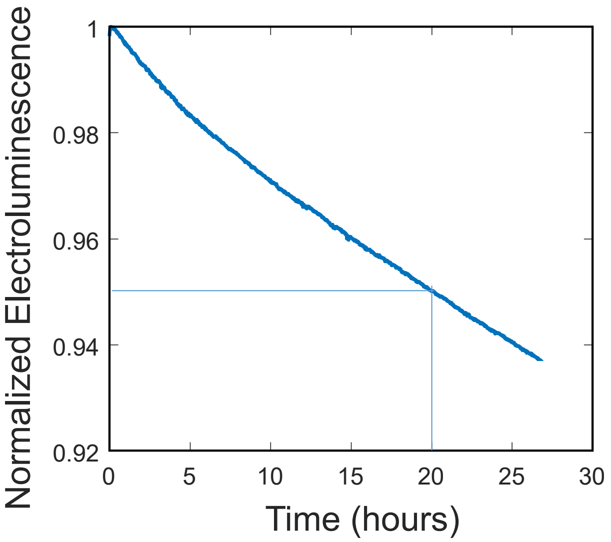

Fig. 7. A stability measurement for a device with a donor-acceptor host, showing a pronounced improvement compared to results shown above. Experiments performed in collaboration with the Jian Li group at ASU.

To explain the results, we consider other species formed in electroluminescence but not modulated by our engineered cathodes. In particular, we probe 'dark' triplet excitons formed in the host or blocking layers. Unlike the phosphorescent emitter, these materials possess weak spin orbit coupling and negligible phosphorescence. Thus, their triplet excited states are 'dark'.

To test for the presence of dark triplets, we compare the OLED's performance when the host material is replaced by a donor-acceptor blend. In addition, we study devices under a weak magnetic field ~ 0.1T. The donor-acceptor blend alters the charge carrier balance but also minimizes the formation of triplet excitons in the host. The magnetic field discriminates between bright and dark triplets. Bright triplets are unaffected by the field of ~0.1T because of significant zero-field splitting caused by the heavy metal atom in the phosphorescent dye. Zeeman splitting of dark triplets, on the other hand, can be appreciable, causing variations in their interaction with charges and other triplets.

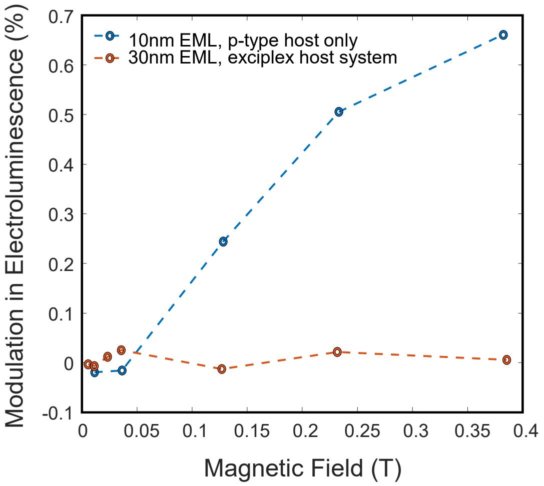

Fig. 8. Magnetic field effect on the EL of a 10nm EML with simple host-emitter system vs 30nm EML with exciplex host system. Both devices have a 30nm ETL and 10nm Ag cathode. With Jian Li, ASU.

First, we characterize an OLED with a donor-acceptor host; see Fig. 7. The stability of the OLED is notably improved, from LT95 = 6.5 hours to LT95 = 21 hours.

The magnetic field dependence is shown in Fig. 8. Dark triplets are observed in the simple host but they are absent in the donor-acceptor host. The magnetic field dependence observed for electroluminescence in the simple host shows a zero crossing at low fields and an enhancement of luminescence at higher fields. The behavior is consistent with a magnetic-field induced suppression of singlet exciton generation from triplet-triplet annihilation. Interestingly, the characteristic shows no evidence of magnetic field-induced modulation of annihilation of dark triplets by charges. Given that the bright and dark triplet densities increase under a magnetic field with no apparent change in γ_{TP}, it is not surprising that we observe a slight increase in degradation rate of the simple host device under a magnetic field, as shown in Fig. 9.

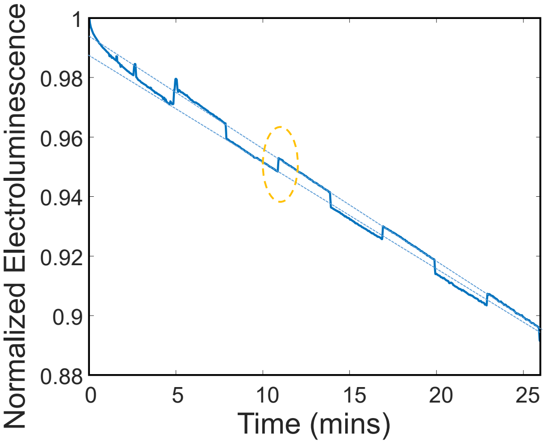

Fig. 9. Degradation of a single host OLED under a switched magnetic field. The brightness increases when the field is on. To visually demonstrate the effect of the field, we extrapolate the slopes of the switched degradation rates at *t* = 11 min. With Jian Li, ASU.

Conclusion

The poor stability of high efficiency phosphorescent blue OLEDs is perhaps the most important fundamental obstacle to the adoption of solid-state OLED lighting. In this work, we have introduced selective probes of bright and dark triplets using coupling to surface plasmons and magnetic field effects, respectively. These probes demonstrate the existence of dark triplet excitons and their role in the degradation of state-of-the-art devices. Destabilizing dark triplets using a donor-acceptor host is observed to substantially improve the stability of blue phosphorescent OLEDs, suggesting that a comprehensive device solution will combine solutions for both bright and dark triplet excitons.

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