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Mapping recombination profiles in single-, dual-, and mixed-host phosphorescent organic light emitting diodes

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ABSTRACT

Recombination dynamics of charge carriers in phosphorescent organic light emitting diodes (OLEDs) play an important role in performance metrics and device optimization even though very little is often known about these processes. In this work, we probe the recombination profile of OLEDs *in-operando* using spatially-positioned sensing layers. This method is used to investigate recombination in the emissive host and transport layer interfaces in a single emissive layer (EML) configuration and is extended to study the impact of double- and mixed-host EML architectures. Devices with the recombination distributed throughout the emissive layer show improved performance metrics, particularly in efficiency roll-off as compared to devices with the recombination pinned at the host/transport layer interfaces.

1. Introduction

Organic light emitting diodes have emerged as a leading display technology owing to their low power consumption, ultra-thin form factor, flexibility, fast response time, and excellent color-rendering properties. The advent of novel phosphorescent active materials has enabled internal quantum efficiencies to reach nearly 100% by utilizing both triplet and singlet excitons. This breakthrough has enabled peak forward emission external quantum efficiencies (EQEs) of more than 30% for green, red, and blue OLEDs [1,2]. However, the efficiency of OLEDs typically decreases at higher brightness and current density due to the reduction of charge confinement and quenching through both bimolecular and exciton-polaron mechanisms [3]. To improve charge confinement in OLEDs, exciton blocking layers have been introduced [4] and bimolecular exciton quenching has been minimized by using phosphorescent emitters with a short exciton lifetime [5,6], reducing molecular aggregation [7] and broadening the exciton recombination zone (RZ) [8–10]. Since the exciton lifetime and molecular aggregation are material specific properties, RZ can be modified by changing the single emissive layer configuration (S-EML) [11] to either a double emissive layer (D-EML) [12–15], a mixed emissive layer (M-EML) [16–19], or a graded emissive layer configuration (G-EML) [20–25]. In addition, single ambipolar host materials with high mobility for both holes and electrons have been demonstrated as an attractive route to modify recombination profiles [26–29].

Experimental determination of the recombination profile can lead to improved performance for OLEDs. Charge confinement and RZ width in OLEDs have been studied by using: 1) sensing layers; 2) quenching layers; and 3) optical modelling. In sensing layer devices, the RZ was qualitatively explored by monitoring the electroluminescence (EL) spectrum of a sensor molecule as a function of position in the device architecture [14,16,25,30–33]. Similarly, the presence/absence of quenching layers have been used as a qualitative monitor of device EL intensity as a function of position in the device [34]. In such devices, mapping of the RZ profile may be produced based on the assumption that EL intensity is proportional to local exciton density at the sensing layer/quenching layer location [35]. The biggest challenge of utilizing the quenching approach is the necessary assumption of exciton diffusion, resonant energy transfer, or electron transfer, complicating interpretation in dilute doped systems. Alternatively, RZ profiles can be indirectly extracted by comparing the EL spectra measured at different angles with optical models derived based on microcavity effects [36], or from variation of the host energetics [37].

In this work, we adapt a method to probe the RZ profiles in OLEDs based on position-dependent luminescent sensing layers internally referenced to the primary emitter EL intensity. To test the generality of the method, a range of device architectures were developed using an *in-silico* approach to characterize potential charge injection barriers.

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Specifically, carbazole and triazine based hosts were predicted to exhibit preferential charge injection from the hole and electron transport layers respectively. The sensor method was used to confirm preferential recombination at the minority carrier interface. The method was subsequently extended to systematically characterize the RZ in various architectures (S-EML, D-EML and M-EML). Our results show that although these structures have only a small impact on the peak quantum efficiency, they play a significant role in the roll-off and power efficiency characteristics of OLEDs at high current densities.

2. Experimental

Devices were fabricated using the device architecture described in Table S1 on pre-patterned indium tin oxide (ITO) (20 Ω-sq.) substrates cleaned sequentially in soap, deionized water, and acetone for 4 min in a sonicating bath then rinsed in boiling isopropanol for 4 min followed by UV-ozone treatment. Thin films were sequentially deposited onto the ITO substrate *via* thermal evaporation at 3×10^{-6} Torr: N,*N*′-bis(naphthalen-1-yl)-N,*N*′-bis(phenyl)-benzidine (NPD, Lumtec) as the hole transport layer (HTL); S-EML, D-EML, or M-EML host uniformly doped with tris[2-(*p*-tolyl)pyridine]iridium(III) ($Ir(mppy)_3$, Lumtec). The S-EML host layer either consisted of 3-(4-(9H-carbazol-9-yl)phenyl)-9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9H–carbazole (E-host, Lumtec) or hole transport host 9,9′-diphenyl-9H,9′H -3,3′-bicarbazole (H-host, Lumtec). The D1-EML host layers consist of E-host:$Ir(mppy)_3$/H-host:$Ir(mppy)_3$ and D2-EML host layers consist of H-host:$Ir(mppy)_3$/E-host:$Ir(mppy)_3$. M-EML host layers consist of blended (E-host:H-host) with varying volume mixing ratio. This was followed by an electron transport layer (ETL) 4,4′-bis(4,6-diphenyl-1,3,5-triazin-2-yl)biphenyl (BTB, Lumtec) and a cathode consisting of 8-hydroxyquinolinolato-lithium (LiQ, supplied by The Dow Chemical Company) and Al. Sensing layer devices were made using platinum (II) octaethylporphyrin layer (Frontier Scientific) inserted at various positions by briefly halting layer growth. Additional experimental details related to the optical and electrical characterization of these devices is provided in the supplemental information.

3. Results and discussion

To investigate the role of emissive layer architecture on recombination dynamics, we fabricated and optimized devices in S-EML, D-EML, and M-EML configurations. The calculated relative HOMO-LUMO energies of each molecule (Figs. S1 and S2) are shown in Fig. 1a along with their chemical structures in Fig. 1b.

The S-EML devices were optimized by changing the concentration of the dopant. The D-EML and the M-EML devices were fabricated by varying the order of the host molecules and the volume-mixing ratio of hosts, respectively. Fig. 1c and d shows the *J-V* characteristics, comparison of current density versus EQE for the fabricated devices and Table 1 summarizes the key performance metrics of the devices. Complete device data is provided in the supplemental information (Figs. S3–S5).

In the S-EML devices, variation in performance follows the trend expected from the injection barriers of the hosts. As seen in Fig. 1a, the E-host has a low energy barrier for electron injection from the ETL as compared with the H-host (0.1 eV and 1.4 eV, respectively). The large electron injection barrier likely leads to poor electron injection into the H-Host, resulting in greater charge imbalance and higher turn on voltage of the S-EML device. In D-EML devices, the order of host deposition was found to play a crucial role in EQE, luminance power and current efficiencies. The placement of an H-Host adjacent to the HTL led to improved current efficiency and power efficiency over devices where the E-host was deposited next to the HTL. Similar to the S-EML device with the H-host, the lower EQE and current efficiency in the E-host/H-host devices resulted from the large energy barrier to electron injection at the H-host/ETL interface. In contrast, improved EQE, current and power efficiencies in the H-host/E-host configuration may be attributed to efficient charge confinement at the H-Host/E-Host interface. Finally, improvements in power efficiency and turn on voltage in M-EML devices likely resulted from the enhanced charge carrier transport and efficient carrier injection achieved by the mixing of the hosts. To validate this, we made hole-only devices using S-EML and M-EML devices. Fig. S6 shows the *J-V* characteristics of the hole-only devices made with single and mixed host layers displaying good symmetry. Hole mobility was extracted by fitting *J-V* curves (Fig. S7) using the space charge limited current (SCLC) model. Mixed host devices showed similar mobility to the H-Host devices and two orders of higher mobility than the E-Host.

To further understand the role of host energy levels on device recombination dynamics, we employed a sensing layer approach. Recombination profiles in the S-EML devices were studied by positioning a thin sensing layer at various locations. The pre-requisite to use sensing layer to probe the RZ zone is that the sensor layer itself should not affect the overall charge transport of the devices. To satisfy this requirement, we employed a sensor layer with high PL efficiency with 0.5 nm thickness to retain the charge transport of the host materials. Our data (Figs. S8 and S9) did not show any trend in current density and turn on voltage of the devices with and without sensing layers indicating the senor layer did not significantly affect the charge transport in the devices. We measured the fraction of sensor emission to the overall device emission at each position of the sensing layer. After deconvoluting any overlap in the emitter and sensor spectra (Fig. S10), we integrate each peak area and normalized the sensor signal by the total device emission (*e.g.* from the data in Fig. 2a and b) *via* Equation (1):

$$F_{Sensor} = \frac{\int \frac{I_{Sens}(\lambda)}{QY_{Sens}(\lambda)} d\lambda}{\int \left(\frac{I_{Sens}(\lambda)}{QY_{Sens}(\lambda)} + \frac{I_{Emit}(\lambda)}{QY_{Emit}(\lambda)} \right) d\lambda} \quad (1)$$

where F_{sensor} is the fraction of sensor photon emission at each position, I_{Sens} and I_{Emit} are the intensity of sensor and emitter component emission respectively, and QY_{Sens} and QY_{Emit} are the quantum yield of the sensor and emitter that are measured to be 30 ± 3% and 94 ± 5%. Because the *QY* and emission peak width of the emitter and sensor are dissimilar, we normalized each signal to obtain the absolute fraction of emission at each sensor position. F_{sensor} is then proportional to the triplet exciton density in the primary emitter stemming from position dependent exciton generation and exciton migration on the host. Some contributions from long-range energy transfer between distant dopants may be present, which will broaden the F_{sensor} profile more than the intrinsic concentration profile, but is likely to be small for these dilute doped systems [38,39]. To validate there is no long-range energy transfer involved between these dopants, we performed PL measurements by inserting an exciton blocking between the primary emitter and the sensor (Fig. S11), and found no long-range energy transfer between the primary emitter and the sensor. Based on this data and the thickness variation seen in our deposition system, we estimate that the resolution of the technique to measure RZ width is around 1 nm. We note that a value of F_{sensor} close to 1 has particular significance (all the emission is seen from the sensor) and implies a discrete position for exciton generation. Accordingly, typical values of F_{sensor} are expected in the range of 0–0.5 if recombination is distributed throughout the host (as opposed to discrete positions or interfaces). A significant benefit of this approach is the use of the primary emitter as an internal reference, negating the need for absolute intensity measurements.

It is important to note that at higher current densities exciton quenching processes such as triplet-triplet annihilation (TTA) and triplet-polaron annihilation (TPA) can play a role in the electroluminescence intensity of the devices made with an emitter that has a longer phosphorescent lifetime [10]. These quenching mechanisms strongly depend on the material properties such as frontier energy levels, triplet diffusion length and local exciton density in the devices. Since the host materials used in this study have higher triplet energy