The different influence of singlet and triplet excitons in the degradation of phosphorescent organic light-emitting devices due to exciton–polaron-induced aggregation of host materials

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ABSTRACT

The lifetime of a phosphorescent organic light-emitting device (PhOLED) may range over several orders of magnitude depending on the choice of the phosphorescent emitter guest material and its concentration. This behavior, we find, results primarily from different rates of exciton–polaron-induced aggregation (EPIA) of the host material due to exciton–polaron interactions. We investigate the influence of singlet versus triplet excitons in the EPIA of host materials and the degradation of PhOLEDs. The results show that there is a correlation between device electroluminescence degradation and the concentration of singlet excitons on the host during electrical driving. In contrast, we find no particular correlation between device degradation rate and the concentration of triplet excitons. The results therefore reveal that singlet excitons play the leading role causing the EPIA of host materials and device degradation by this mechanism.

1. Introduction

Organic light-emitting devices (OLEDs) are starting to be utilized in flat panel displays and solid-state lighting [1]. With the emergence of organometallic phosphorescent emitters and the development of phosphorescent OLEDs (PhOLEDs), very high electroluminescence efficiencies are now possible [2,3]. Due to strong spin–orbital coupling in these emitters, radiative relaxation of both singlet and triplet excitons becomes possible, allowing the realization of devices with almost 100% internal quantum efficiency [2–4]. In PhOLEDs, the phosphorescent emitters are typically doped into a host material at a low concentration (typically <10% by volume).

Despite the significant progress in their development, PhOLEDs, especially blue-emitting ones, generally have a relatively limited electroluminescence (EL) stability. Their lifetimes, defined as the period of time it takes for device EL intensity to decease to a certain percentage of its initial level under constant current driving, continues to be much shorter in comparison to their fluorescent counterparts [5]. A root cause of their faster degradation, we recently found, is the occurrence of exciton–polaron-induced aggregation (EPIA) in the wide-bandgap (E_g) host materials [6]. This previously unknown molecular aggregation behavior is induced by interactions between excitons and positive polarons that reside on host molecules during electrical driving and affects wider E_g materials more significantly [6,7]. Whether the excitons involved in driving this aggregation mechanism are mostly singlets or triplets has however remained unclear.

In this study, we investigate the roles of singlet versus triplet excitons in the EPIA of wide-E_g host materials in PhOLEDs. The results uncover a correlation between EL degradation rate and the concentration of singlet excitons on the host during electrical driving. In contrast, we find no particular correlation between device degradation rate and the concentration of triplet excitons. The results therefore reveal that singlet excitons play the leading role causing the EPIA of host materials and device degradation by this mechanism.

2. Experimental section

For the PhOLEDs used in this work, we use 4,4′-bis(carbazol-9-yl)biphenyl (CBP) as both a hole-transport material and emitter host, and 1,3,5-tris(N-phenyl-benzimidazol-2-yl)-benzene (TPBi) as an electron-transport material. Tris(1-phenylisoquinoline)iridium (Ir(piq)$_3$) and platinum octaethylporphine (PtOEP) are used as phosphorescent guests, doped into the CBP host by co-deposition. Indium tin oxide (ITO) and aluminum (Al) are used

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as anode and cathode, respectively. All devices are fabricated by the deposition of the organic materials and metals at a rate of 1 Å/s using thermal evaporation in vacuum at a base pressure of about 5×10^{-6} torr on ITO-coated glass substrates. An Edinburgh Instruments FL920 spectrometer is used for time domain fluorescence lifetime measurements. An Ocean Optics QE65000 spectrometer is used for the measurements of device EL spectra. All tests are carried out in a N_2 atmosphere in order to avoid effects arising from ambient environments.

3. Results and discussion

3.1. Device EL degradation due to host EPIA

We first study the degradation behavior of PhOLEDs with various concentrations of Ir(piq)$_3$ or PtOEP as guest materials. The general structure of the devices is ITO(120 nm)/MoO$_3$(5 nm)/CBP (20 nm)/CBP:Guest(1.5% or 5% by volume, 20 nm)/TPBi(30 nm)/ LiF(0.5 nm)/Al(100 nm). Fig. 1 shows EL intensity (normalized to the initial values) and ΔV (defined as the driving voltage, V_d, at the given time minus the initial value) versus time during which these devices are driven by a constant current of density 20 mA/cm^2. The initial brightness values of the devices containing 1.5% PtOEP, 5% PtOEP, 1.5% Irpiq and 5% Irpiq are 170, 260, 2200 and 1800 cd/m^2, respectively. The initial V_d values of these devices are 7.8, 8.4, 8.1 and 8.0 V, respectively. As the figure shows, the Ir (piq)$_3$ devices exhibit much higher EL stability (longer device lifetime) relative to the PtOEP devices, despite the fact that the devices utilize the same host and charge transport materials, an observation that shows the strong dependence of device stability on the guest material species. Although the initial brightness of the Ir (piq)$_3$ devices is significantly higher than that of the PtEOP devices, their stability is also higher, contradicting the commonly accepted notion that the rate of device degradation is proportional to its initial brightness. Considering that Ir(piq)$_3$ and PtOEP are both red emitters with very similar energy gap [2,8], the significant difference in device stability is somewhat surprising, especially that red phosphorescent guests are perceived to be very stable in general [9]. Moreover, as shown in the figure, for the devices with the same guest, an increase in guest concentration (e.g. from 1.5% to 5%) leads to an increase in device lifetime. This cannot be explained by previous suggestions that the EL loss is mainly due to molecular decomposition/dissociation of the guest materials [10]. Such variation in device lifetime with guest concentration also suggests that the heat produced in the devices as a result of the current flow may
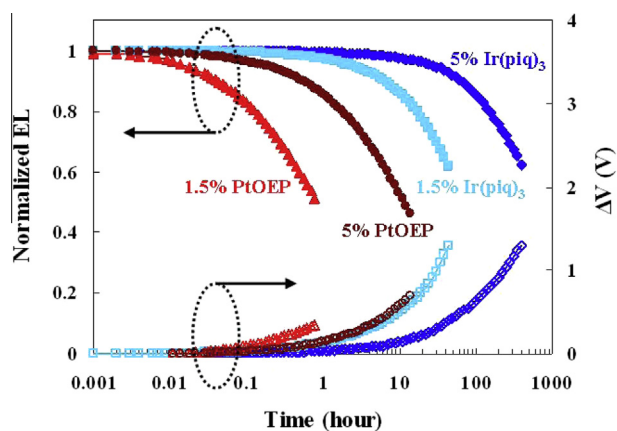
not be a major cause for the observed device degradation, as the EL efficiency of the devices with the same guest species but different concentrations is generally very similar, indicating that energy losses in the form of heat must also be comparable.

The observations are however consistent with our recent findings that PhOLED degradation is primarily caused by the EPIA of the wide-E_g hosts (i.e. the CBP host in this case) [6]. Fig. 2 shows EL spectra (normalized to the peak EL intensities of the guests) of the devices in Fig. 1 collected before (i.e. from the fresh devices) and after the electrical stress (i.e. after the device EL has decreased to 70% of its initial value). Clearly, the spectra correspond to the characteristic luminescence spectra of the guest materials Ir(piq)$_3$ (i.e. Fig. 2(a) and (b)) and PtOEP (i.e. Fig. 2(c) and (d)). A closer examination of the spectra (the enlarged spectra in the insets) however reveals a small amount of blue EL from CBP singlets with a peak at ~400 nm in all devices and, in case of the PtOEP devices, an additional smaller band at ~545 nm which can be attributed to EL from higher level of thermally populated PtOEP triplet states [11]. What is however more remarkable is that all the devices show some spectral change after the electrical stress (can be seen in the differences between the red and black traces in the insets). For example, the 5% Ir(piq)$_3$ device exhibits very small (but detectable) spectral changes after 260 h of aging, whereas the 1.5% Ir (piq)$_3$, 5% PtOEP and 1.5% PtOEP devices show more significant spectral changes after only 31, 3.4 and 0.25 h of aging, respectively. As the insets show, the spectral changes mainly occur in the 400–600 nm region, and correspond to the emergence of a new band with a peak at ~500 nm, which can be attributed to emission from CBP aggregates as a result of the EPIA process [6]. It should be pointed out that the CBP aggregation also occurs in PhOLEDs containing green and blue emitters. Detecting them is however more difficult in this case because of the overlap of the aggregate luminescence with luminescence from the green/blue emitters. This is the main reason for using red emitters as the guest materials in this study. Fig. 3 shows a plot of device lifetime (defined here as the time elapsed until the EL decreases to 70% of its initial value) versus the host aggregation rate (defined as the intensity of the host aggregate emission band in the EL spectra divided by the time of electrical driving elapsed, which approximately reflects how fast the host EPIA takes place in the devices). As the figure shows, there is a clear correlation between the two attributes where devices with shorter lifetimes have higher host aggregation rates, indicating that device EL degradation is indeed closely linked with the host EPIA rate. In this regard, the differences in the lifetimes in Fig. 1 can be attributed to different host EPIA rates in the different devices. It is noteworthy to point out that EPIA also occurs to guest materials, especially wide-E_g ones (i.e. blue-emitting emitters) [12], however, EPIA of narrow-E_g guests (i.e. red-emitting emitters) such as Ir(piq)$_3$ and PtOEP is found to be negligible in comparison with host EPIA in the time frame of our experiments here [12]. Therefore, the device degradation behavior exhibited in Figs. 1 and 2 can be primarily attributed to host EPIA.

3.2. Investigating the influence of singlet excitons in host EPIA

In general, both singlet and triplet excitons are present in high concentrations in the devices during operation. In order to determine if one of the two types of excitons plays a more significant role in the observed EPIA and PhOLED degradation, we first study the effect of singlet excitons. As host singlets dissipate their energy radiatively in general, we first study EL from the host to estimate the relative amounts of host singlets present in the various devices when under electrical driving and see if they may correlate with device stability. Fig. 4(a)–(d) shows EL spectra (normalized to the peak EL intensities of the guests) collected from the fresh devices in Fig. 1 driven at current densities of 20, 2 and 0.2 mA/cm^2. All

Fig. 1. EL intensity (normalized to initial values) and ΔV versus time during which PhOLEDs containing Ir(piq)$_3$ and PtOEP as guests are driven by a constant current of density 20 mA/cm^2.