Reversible Shift from Excitonic to Excimer Emission in Fluorescent Organic Light-Emitting Diodes: Dependence on Deposition Parameters and Electrical Bias

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ABSTRACT: Organic light-emitting diodes (OLEDs), in general, require multilayer devices and microcavity structures for emission tuning, which increases the complexity and cost of production. Hence, it is imperative to develop techniques for spectral tuning, which employ simplified device structures. In this study, we have selected a tris(8-hydroxyquinolinato)aluminum (Alq₃): 10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-(1benzopyropyrano (6,7-i,j)quinolizin-11-one (C545T)-based OLED and investigated the dependence of the OLED emission on various deposition parameters and the electrical bias. The concentration of the dopant in the emissive layer (EML) was varied from 3 to 50%, and the single dopant emitter as a limiting case was also studied along with studies on the varied deposition rates and EML thickness. By varying the deposition parameters, the emission was observed to change from excitonic green to excimeric yellow. With increased doping concentration, reduction in pure exciton emission with an increase in excimer emission was observed, resulting in electroluminescent spectral red shift. Similarly, electroluminescence spectra have shown different levels of broadening, depending on the deposition rate and thickness of the EML. These effects could be reversed with increasing applied electric field. Thus, it is indicated that, by suitably optimizing the deposition parameters of the dopant material, spectral tuning can easily be obtained, which may form the basis of simplified and cost-effective device structures.

INTRODUCTION

The first reported organic light-emitting diode (OLED) with a doped emission layer (EML) consisted of tris(8-hydroxyquinolinate)aluminum (Alq₃) as the host and a coumarin derivative and DCM (4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran) as the dopant.¹ Doping the Alq₃ host with a suitable dopant is found to cause considerable gain in electroluminescence (EL) efficiency as well as in device lifetime. In a host-dopant matrix, carrier transport properties can also be tuned separately. The optimal dopant concentration in fluorescent OLEDs is found to be typically below 5%. At a low dopant level, an excited state complex or exciplex, which is only bound to the excited state, can form between the dopant dye and the host material in the host-guest matrix due to the charge transfer or energy transfer from either host to guest or vice versa. On the other hand, with increased dopant concentration in the host-guest matrix, a decrease in emission intensity and red shift to the emission peak was observed, which was attributed to a possible excimer emission.¹ As the dopant concentration increases, dye molecules begin to form aggregates, leading to self-quenching and thereby emission loss. This can often comprise the nonemissive excimer formation, where the exciton is delocalized over two dopant molecules.² The dimer formed in the excited state is not bound to the ground state and dissociates upon relaxation. The emission from the excimer, if any, generally would have the characteristics of low quantum efficiency and a broadened emission spectrum.

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Coumarin dye and its several derivatives have been in use for a long time in the case of flash lamp pumped organic lasers. After the introduction of the guest-host emitter system in OLEDs, a few coumarin derivatives started appearing as dopants in the Alq3-based host system, which made it one of the earliest group of dopants used in OLEDs for efficient emission, for example, 3-(2-benzothiazolyl)-7-(diethylamino)-2H-1-benzopyran-2-one, known as C-6, which fluoresces at a peak wavelength of 505 nm in EtOH with a 78% photoluminescence quantum yield. The quantum efficiency was enhanced up to 90% when the C-6 structure was modified to 10-2-benzothiazolyl]-2,3,6,7-tetrahydro-1H,5H-benzo- l]pyran[6,7,8-i]quinolizin-11-one or C545T, and the emission is red-shifted to 519 nm. However, its planar structure caused more aggregation in the solid state as evidenced by the presence of a long wavelength shoulder in the photoluminescence (PL) and EL spectra at high concentration. Introducing four methyl groups in C545 to reduce the dye–dye interaction at high concentration led to 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H-benzo[l]pyran[6,7,8-i]quinolizin-11-one or C545T, which became the most commonly used green dopant for Alq3 due to its high luminance efficiency, unique hue, and less concentration quenching compared to other derivatives. The OLED emitter with 1% C545T doped with Alq3 is reported to have a current efficiency of 10 cd/A. A doping concentration of 2% C545T has recorded very fast energy transfer and maximum PL efficiency in a study, where the doping concentration is varied from 1 to 5%. Increasing the dopant concentration up to 7% resulted in the dopants forming aggregates and red-shifted EL spectra, along with reduced radiative decay rate and increased nonradiative decay rate, suggesting strong nonradiative recombination. On increasing the dopant concentration further up to 23%, yellow emission with Commission Internationale de l’Eclairage (CIE) coordinates of (0.45, 0.53) was obtained compared to the (0.29, 0.66) for a dopant concentration of 1%. This red shift in the emission spectrum is attributed to the C545T excimer formation and corresponding emission at high dopant concentration.

The dopant emission in a host-dopant emissive system is explained as the host to guest energy transfer or the direct dopant recombination due to carrier trapping. The highest device performance was obtained by doping of Alq3 with low C545T concentration. However, once the dopant concentration increases, the dopant monomers may aggregate to form dimers, and the excited state energy transfer due to dipole–dipole interaction between the dopants may increase. This may cause excitons to be trapped in the aggregates without any reverse transfer to the monomer molecules. This can lead to a radiationless relaxation or a different radiative relaxation path, causing fluorescence quenching. Rhee et al. studied a relatively high doping concentration of the Alq3:C545T system by considering C545T molecules as charge carrier traps. The C545T single emitter devices fabricated with EML thicknesses of 30 and 120 nm gave evidence to heavy self-quenching. Whereas the thinner EML device gave a broad spectrum with a peak at ~573 nm, the 30 nm-thick EML device exhibited weak C545T exciton emission with a peak at 530 nm along with strong excimer emission. Thus, the previous studies have confirmed the change in nature of excitons from excitonic to excimer when the dopant concentration is increased. This is an important observation as the resulting spectral shift can be utilized in tuning the OLED emission with a simplified device stack. This potential can be extended to design and fabricate efficient white OLED with reduced process complexity. Nevertheless, the dependence of this emission tuning on the electric field, rate of deposition, and thickness of the single dopant emitter layer along with different concentrations of the dopant in a host-guest system has not yet been systematically studied. Herein, we study the effect that the doping concentration is having on the optoelectronic properties of C545T:Alq3 matrix up to a maximum doping of 50%. C545T as a single emitter, deposited with varying deposition rates as well as varied thickness and its effect on the resultant excimer emission along with its field dependence, is also studied. The Alq3:C545T system is chosen as it is a well-studied system with most of the material properties already known. There is still a lot of research interest in this emitter system evinced by several recent publications.

**RESULTS AND DISCUSSIONS**

There are numerous studies focused on finding the optimized doping concentration in different EML host-guest units to ensure efficient energy transfer between the host and the guest. As mentioned in the Introduction, efficient transfer requires very low dopant concentration. Nevertheless, there are not many reports concentrating on increased dopant concentration, and the majority of them study up to 10–20% dopant concentration range. These were aiming at studying triplet–triplet annihilation (TTA) effects or confirming excimer emission without any other detailed investigation. The study by Rhee et al. reporting a thick C545T single emitter, confirmed the excimer emission and studied the charge trapping. They have studied different percentages of doping up to 6% and also single emitter devices with two different thicknesses. This is a detailed study in which the authors probed the change in exciton formation route from the Förster transfer to direct charge trapping. However, they have studied only 30 and 120 nm thicknesses for single emitter devices, and no dependence on deposition rate has been investigated. Since the deposition rate can affect the molecular packing, it can, in turn, influence the excimer emission as well. Ultimately, the effect of the electric field on devices with varied doping concentration and single emitter devices with varied thickness and rate of deposition needs to be studied to complete the picture. In this work, we have systematically studied the effect of increased doping concentration on the Alq3:C545T system starting from 3 up to 50%. As a limiting case of this high doping concentration, we have also studied the C545T single emitter system under different deposition conditions. Keeping the EML thickness constant, we have changed the C545T evaporation rate from 0.1 to 5 Å/s. After optimizing the device for the rate of deposition to extract maximum emission, the EML thickness is varied in the subsequent part of the study. These investigations provide further information on the Alq3:C545T system, which we believe can be a building block for simplified OLED structures.

**Alq3:C545T System Effects of Heavy Doping.** Figure S1 shows that the OLED device structure was fabricated to study the effect of dopant concentration in EML. Here, OLEDs are fabricated with Alq3, doped with C545T as the emitter. The device structure is as follows. ITO/N,N’-bis(naphthalen-1-yl)-N,N’-bis(phenyl)-benzidine (NPB) (40 nm)/Alq3; x wt % of C545T (30 nm)/Alq3 (35 nm)/LiF (1 nm)/Al, where x = 3, 10, 20, and 50%. As the level of doping increases, a
proportional increase in the current density can be expected. However, interestingly, this is not the case, as shown in Figure 1a. Current density reduces when the doping is increased from 3 to 10%. This is recovered when the doping is at 20% and then increases further by 50% doping. This is not the trend followed by the luminance, which steadily decreases with an increase in doping, as shown in Figure 1b. The same trend is followed by the current efficiency, as shown in Figure 1b. It is already reported that the current density increases with dopant concentration, at low doping concentrations. As the doping concentration further increases, the emission mechanism changes from excitonic to excimer, and hence, the current density and luminescence both decrease. However, above 10% doping, the hole transport nature of C545T becomes dominant, and hence, the total current increases. However, there is no consequent increase in luminescence because the excimer emission is not very efficient.

Going up to 10%, current efficiency is reduced by half and is further reduced with an increase in doping. The variation of current efficiency with current density is also worth studying. The current efficiency increases with current density for 3% doping, which indicates the enhancement in emission due to the TTA effect, as suggested by Luo and Aziz. For the 10% doped device, the current efficiency remains almost constant upon increasing the current density. Above 10% doping, no effect of TTA is previously reported. So, the effect of TTA can be expected not to influence the emission of OLED with heavy doping of C545T. Corroborating this observation, the current efficiency, in fact, decreases with increasing current density for 20 and 50% doped devices, as can be seen in Figure 1b.

The change from the expected trend in current density can be attributed to the change in carrier injection capabilities with variation in the doping level. When doping increases, along with aggregation, there may be a change in dipole–dipole interaction locally. This change in polarization can reduce the band gap, which makes the excimer emission at long wavelength unpredictable due to the interplay of several mechanisms. The variation of external quantum efficiency with current density is given in Figure S2, which also shows more or less the same trend as that of current efficiency. The variation of power efficiency with operating voltage is shown in Figure S3. The power efficiency is also seen to be decreasing with increased dopant concentration, which is expected as the luminescence at a given voltage is lesser for heavily doped samples.

However, it may be noted that these devices are not in the standard OLED architecture with hole injection, electron blocking, hole blocking, and doped transport layers. Hence, efficiency values are expected to be low, while we are more interested in the emission spectrum.

Figure 1c shows the PL spectrum of 5 and 50% C545T-doped Alq3 thin films. When the doping concentration increases, the 574 nm shoulder in the 5% doped film, which is due to excimer emission, becomes dominant compared to the 528 nm peak, which is the excitonic emission. This relative intensity difference between the two peaks of emission spectra for the two differently doped films can be attributed to the aggregation-induced effect of the C545T molecule in the film.
The C545T dopant concentration in Alq3 host thus has a keen effect on the EL spectrum as well as the device efficiency. With the increase in doping concentration, the spectrum is red-shifted along with a distinct decrease in device efficiency. This is also evident from the normalized thin film PL spectra attributed to the excimer emission of the dopant. It is well established that electroluminescence and photoluminescence may not be identical since the former is basically an optical property, whereas the latter involves several electronic properties as well. We have earlier reported that the major part of the recombination happens near the HTL/EML interface due to piling up of holes near this interface.25 In PL, we might be able to tap all the excimers, whereas in EL, only the excimers near the HTL/EML interface can lead to excimer emission; thus, excitonic emission may still dominate. Carrier trapping, which might happen, may also be confined near the interface due to the low hole mobility of Alq3. The C545T clusters away from the interface are not getting a chance to get excited either by trapping or by direct energy transfer. The relatively narrower EL spectrum points to a weak microcavity effect also because the latter has been used to enhance color purity by narrowing the emission spectrum.20

In the electroluminescence spectrum in Figure 1d, when the dopant concentration is varied from 3 to 10% and then to 20%, there is a slight widening of the spectra and it is red-shifted as well. The 574 nm shoulder is attributed to the excimer emission as per the previous reports.11−14 It may be noted that there is one report suggesting this red-shifted emission to be due to the Förster transfer.13 The excimer emission is usually bathochromically shifted compared with usual fluorescence so that there is almost no overlap between the emission and absorption. To verify this, we studied the absorption and emission of C54ST films and found out that there is very little overlap. Comparison of PL emission and absorption of the C54ST film is provided in Figure S4. Also, we have fabricated C54ST-only devices, and they also showed this red-shifted emission around 574 nm (also shown in Figure S4), which indicates that it has excimer origins, as shown in the subsequent section. This 574 nm emission is not as distinct in EL as it is in PL.

The relative intensity between the peak and the shoulder decreases with doping. When doping goes from 3 to 50%, the relative intensity is almost halved. Up to 10% doping, quenching increases. However, above 10%, even though direct capture of charge carriers increases as proposed by Rhee et al.,16 the increase in local current density only contributes toward the nonradiative recombination current, Jnr. Therefore, the charge balance also deteriorates for heavily doped devices. Here, the charge imbalance and the nonradiative pathway compete with the excimer pathway.

With the increase in doping percentage, luminance decreases as expected. This is attributed to the concentration quenching due to dye molecule aggregation. As can be seen in Figure S5 and Figure 2a, CIE (x, y) coordinates are shifting toward the yellow region from green with an increase in doping concentration. When the external bias is increased, the CIE coordinates tend to return to the green region as indicated in the CIE chart. This indicates the decreased emission from the aggregate with an increased applied electric field. It may also be due to the field induced dissociation of the aggregate, as suggested by Wortmann et al.27 As the charge carriers can easily overcome the energy barrier at the higher applied electric field, the probability of charge transfer may increase, leading to fast exciton dissociation. Another reason for this blue-shifted emission at higher fields may be the generation of high energy excitons, as proposed by Shao and Yang.28
Field dependence of color coordinates is seen to increase with doping concentration. At heavy doping, the emission mechanism follows a different pathway. However, even this change in the favored pathway is influenced by bias voltage, as shown in Figure 2b. Apparently, for the heavily doped device, with increased bias, the emission tries to revert to the 3% emission range, which is the new predominant emission mechanism with the excimer weakened. However, direct capture may prevail. The polarization effects are diminished at high bias along with the reduced excimer emission. Excimer dissociation, as well as reduced charge balance or generation of high energy excitons, may be the reason. The reduction in the 574 nm shoulder at high bias is prominent in a 50% doped device, as shown in Figure 2c.

Increasing dopant concentration and decreasing the band gap may decrease electric field-induced fluorescence quenching.29 When the current increases, charge carrier-induced quenching is also possible. With the decrease in the band gap, field-induced quenching decreases. By narrowing the energy gap, the excited states are less prone to dissociation. Aggregation may reduce the band gap as previously reported, and hence, quenching decreases initially with a small increase in doping concentration.27 However, with the further increase in concentration, trapping increases, which supports non-radiative pathways. An increase in current density without a corresponding increase in luminance can be explained as above.

Above a certain percentage of doping, concentration quenching and luminescence due to direct charge trapping compete with each other. The 3% doped device exhibits an excellent charge balance using the direct excitation and energy transfer mechanisms. In the case of 10% doping, current density decreases because of the enhancement in charge trapping. For 20% doping, aggregation changes the band gap and assists in carrier transport. The same phenomenon continues with 50%, and current increases due to direct injection into C545T, which does not contribute toward luminescence due to concentration quenching. Thus, aggregation is perceived to be playing a role in defining the optoelectronic properties of these devices. In a solution, we can study aggregation by increasing the concentration, but in a thin film, which is already a condensed formed, the only way to change the packing is by changing the deposition rate. Hence, we further studied a variation of the rate of evaporation of C545T in a single emitter device.

**C545T Single Emitter.** I. Effect of Variation of the Evaporation Rate of C545T. There has not been any comprehensive study on the effect of evaporation rate on C545T single emitter devices. The available works only confirm the presence of excimer emission at higher doping.16 Effect of aggregation whatsoever is expected to be aggravated at a higher evaporation rate. Accordingly, as the rate increases, the shoulders in the doped devices are expected to broaden. The polarization effects also should become maximized. Here, we are studying the C545T single emitter as a limiting case of high doping. A single layer of C545T with a thickness of 30 nm is deposited as the emission layer (EML) of OLED at rates of 0.1, 2, and 5 Å/s. The PL emission from the C545T thin film is compared with PL emission from C545T solution also. Figure 3a shows the PL spectrum of C545T in solution (chloroform) and for a neat film of 30 nm thickness. The 503 nm peak wavelength for the C545T emission in solution is shifted toward ∼586 nm for the neat film deposited at a rate of 2 Å/s. Both the solution and film have a shoulder at 532 nm. As mentioned in the previous section, this red shift of the major peak may be attributed to the excimer formation of the C545T...
dye. There is also a possibility of a solid-state solvation effect, which can cause a spectral red shift induced by the change in local polarization and thereby the local electric field.\cite{24,30} Due to the close packing, the C545T molecule can self-polarize, thereby increasing the local polarization field. This polarization also can contribute toward the red-shifted spectrum. Unlike in the case of the Alq3:C545T emitter, all the C545T molecules are surrounded by the neighboring C545T molecules themselves. This makes the spectrum slightly more red-shifted compared to the Alq3:C545T 50% doped layer.

From the electroluminescence spectra in Figure 3b, the EL spectrum of each of the C545T single emitter OLED peaks at a wavelength of 532 nm, the shoulder peak in the PL spectra. Nevertheless, on increasing the deposition rate, the spectrum widens toward a longer wavelength. This can only arise from the difference in the molecular packing due to the change in deposition rate. Slow deposition can lead to nonstructured defects and trapping. Therefore, the effect of self-polarization might be less at a low deposition rate. So, the red shift can be comparatively less in this case. However, the device having EML deposited at a 2 Å/s rate shows the maximum emission intensity. On further increasing the rate, the luminescence is reduced. Both of the devices with EML deposited at 2 and 5 Å/s show similar current densities, while the device of 0.1 Å/s deposited EML exhibits a poorer performance. The latter can be attributed to poor morphology of the EML. The CIE color chart in Figure 3c also shows a similar trend with EML of 0.1 Å/s, leaning toward a hue that is more greenish. Both the other devices show closer CIE coordinates following the trend in EL spectra and J−V−L characteristics with a more yellowish emission resulting from the broadening of the spectrum.

Whereas the emission of the 0.1 Å/s device is located more or less in the yellow-green edge in the CIE chart with a dominant contribution from green, 2 and 5 Å/s devices are giving yellow emission, as evidenced by the CIE coordinates in Figure 3c. These CIE coordinates of the 0.1 Å/s device remain almost the same in the whole range of biasing voltage. Even with this kind of color stability, the 0.1 Å/s is showing very poor device performance, as shown in Figure 3d. It has recorded a very low current density as well as luminance. This may be due to the poor film connectivity. Charge transport in thin films has been studied with respect to the effects of electric field, temperature, dopant concentration, film morphology, etc. on charge carrier mobility as well as device functioning. The evaporation rate is definitely going to affect the morphology and thereby electrical and optical properties.

For example, Lee et al. have reported the variation of current density of Alq3 films as a function of rate.\cite{31}

In addition, there are several reports detailing the effect of micro- and nanostructural changes emerging from various morphologies on charge carrier transport from Qiao et al.,\cite{32} Liu et al.,\cite{33} and Ramos et al.\cite{34} We are proposing that varying the deposition rate changes the molecular packing and film morphology and thereby the device performance.

However, for the higher rates, they tend to move toward the green region in the color chart. These can also be observed in the color coordinate plot given in Figure S6. This is also evidenced by the normalized EL spectra at different bias voltages in Figure 4. The EL spectrum for 0.1 Å/s remains the same for all voltages, but for the other two higher rates, the same spectrum is narrowing at the longer wavelength region with an increase in voltage.

As the polarization effects are minimum, color coordinates remain unchanged with voltage indicating the absence of any reversible conformation changes. The poor morphology of 0.1 Å/s also brings about a large number of traps in the layer. The presence of traps without the smooth connectivity between the molecules is substantiated by the slight increase in current density with a negligible enhancement in luminance when the driving voltage is increased. Due to its conformational weakness, charge carrier mobility in the layer does suffer. This badly affects the charge balance in the structure. The connectivity issues and absence of any local polarization effects cause a virtual depletor effect, and the possibility of an electron−hole pair is reduced. The fraction of dimers formed on deposition of the layer may emit relatively weakly, but the exciton emission is the only pathway that gets benefited by the increase in carrier injection due to the increase in voltage, which is again negligible. All other aggregate excited states follow a nonradiative pathway with an increase in the electric field. Only a minimal number of excitons and excimers are formed, and the dominant fraction of them relaxes non-radiatively.

On the other hand, 2 and 5 Å/s devices show comparable current density and luminance with 2 Å/s having the relatively high luminance. However, the EL intensity plot shows a very distinct intensity variation, even though the spectrum is similar. That is, the 2 Å/s device favors efficient radiative recombination. Both of the devices have an EL spectrum, which broadens on longer wavelengths and narrows with voltage. With a high enough bias, it may give a clean enough emission spectra like 0.1 Å/s. This broadening in the emission...
indicates the presence of excimer emission, which again is being suppressed with the increase in voltage. The packing in the 2 Å/s film seems to provide more radiative recombination centers. The 2 Å/s film is probably having more trap-assisted recombination due to its relatively loose packing compared to the 5 Å/s film. This combined with the improved carrier mobility for holes due to better connectivity may reduce the charge carrier balance for the 5 Å/s device.

II. Effect of Variation of C545T Thickness.

The device with EML deposited at 2 Å/s was found to be the most efficient in the previous section, and now, the next part of the study is to find out the effect of different thicknesses on the emission. The EML thickness is varied to be 10, 20, 30, 60, and 70 nm. The device structure remains the same. As the hole blocking on the ETL side is negligible, a lesser EML thickness can cause the exciton recombination zone to be shifted toward ETL. Device characteristics with the increase in thickness are shown in Figure 5a. The current density decreases initially, as is expected. However, this enhancement in current density is not getting proportionally translated to luminescence. Therefore, this increase in current density contributes toward a nonradiative recombination current. The luminescence in general also decreases with an increase in thickness, the only exception being the 30 nm device. This can be associated with a weak microcavity effect in this configuration. This is evidenced by the EL spectra of the same in Figure 5b.

In the normalized EL spectrum recorded at 8 V, the devices with EML thicknesses of 10 and 20 nm have a peak wavelength of 532 nm with an ∼565 nm shoulder. This 565 nm shoulder peak is higher for the 20 nm device. The 30 nm device has a comparatively narrower spectrum with a peak wavelength of 532 nm. It also has the highest spectral intensity. This may be due to the weak microcavity effect at this 30 nm optimized EML thickness. For the 60 nm device, the EL peak is slightly shifted to 536 nm with a strong shoulder at 562 nm. This trend is followed by the 70 nm device, whose total broadening of the spectra and the strengthening of the shoulder result in a 560 nm peak.

The effect of this EL spectra shift and broadening is distinct in the CIE chart in Figure 5c. With the increase in EML thickness, the CIE (x, y) coordinates are moving toward the yellow region with the 70 nm device tending toward a yellowish-red color. The latter exhibits a pure yellow hue and the weakest luminance for a given current density (Figure 5a). The 30 nm device has the maximum luminescence intensity with all others falling in between. It is obvious that, as the EML thickness increases, the C545T pure excitonic emission decreases, and excimer excitation increases as evidenced by the change in the relative intensity between initial 532 and 565 nm peaks, the peak shift, and broadening. Along with the molecular structure and doping concentration, excimer emission depends on charge carrier transport as well. This can influence the excimer recombination. So, the charge carrier mobility and the local carrier density can help to improve the excimer emission by reducing C545T emission. This is in congruence with the observation in the previous section.

The 10 nm device shows C545T exciton and excimer peaks. When thickness increases, the C545T exciton and excimer emission become comparable at 20 nm. However, for the 30 nm device, both of the emission intensities increase, but the exciton peak is visibly dominating. This may be due to a weak microcavity effect as discussed previously. Nevertheless, the 60 nm device shows a reduced excimer emission, and the 70 nm device has both peaks with equal intensity. It should be recalled that Rhee et al. have reported a very weak excitonic...
and strong excimer emission for a single emitter device with 120 nm thickness of C545T. Combining this with our result, it can be understood that, beyond 70 nm, the excimer peak starts dominating. As can be seen in Figure 5c and Figure S7, the emission tries to revert to green emission at high electric bias for all the range of thicknesses studied.

The current density decreases with an increase in thickness of up to 30 nm due to the resistive contribution. For the 60 nm device, the current density is slightly increased. However, the 70 nm device has reported the highest current density. As the thickness increases, C545T molecules are grown on a previously deposited C545T layer, passivating the defects and reducing the traps, which could be the reason for the slightly higher current density exhibited by the 60 nm device compared to that of the 30 nm device. This trend is continued for the 70 nm device, which exhibits the highest current density.

Normalized EL intensities for the OLEDs with different EML thickness and the driving voltages of 6, 7, and 8 V are given in Figure 6. The peaks corresponding to 10, 20, and 30 nm are 532 nm, and for 60 nm, it is 536 nm. For the 10 and 20 nm devices, the 564 nm shoulder in the peak can be found to be decreasing with applied voltage. This can be associated with the effect of applied electric field on the excimer emission as discussed in the previous sections. However, as it is absent in the thick EML device, it could be due to the lesser effective applied field. For the devices with an EML thickness of 30 nm and above, the normalized EL spectra are unchanged when the applied voltage is changed from 6 to 8 V. Therefore, the contribution to exciton formation remains the same even at a high applied voltage, which could be the direct charge trapping by the C545T molecule (532–536 nm) and excimer emission (564 nm). A summary of the emission characteristics is given in Table 1.

It may be noted that, though heavy doping leads to concentration quenching in the present case, approaches such as using two hosts having twisted structures with high steric effects have been used to prevent intermolecular aggregation and to reduce luminescence quenching.36

Figure 6. Normalized electroluminescence spectra of the OLEDs for different EML thickness and operating voltage: (a) 10, (b) 20, (c) 30, (d) 60, and (e) 70 nm.
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inserting a blue emitter.

emission with this simple stack design can be explored by peak and spectral broadening. Here, potential for white could be tuned between yellow and green by shift in emission spectra, and by controlling them for the EML, OLED emission change in deposition conditions can significantly in the device structure.

Thinner layers result in different emission characteristics due to different deposition rates. High evaporation rates alter the molecular packing of the emissive species, and thus, the red-shifted excimer emission is proven to be arising out of aggregation-induced effects. We have also fabricated dopant-only single emitter devices with different thicknesses and found that, for a device with a 70 nm thickness, the contributions from excimer and excitonic emissions are almost equal, yielding a broad emission spectrum. In this study, it has been demonstrated that the change in deposition conditions can significantly influence EL spectra, and by controlling them for the EML, OLED emission could be tuned between yellow and green by shift in emission peak and spectral broadening. Here, potential for white emission with this simple stack design can be explored by inserting a blue emitter.

EXPERIMENTAL SECTION

Indium tin oxide (ITO)-coated glass substrates (Kintec Company, Hong Kong) were cleaned in a liquid detergent solution (Alkanox) and subsequently sonicated in deionized water and 2-propanol. After drying, the UV-ozone-treated (Novascan) substrates were loaded into the thermal evaporation chamber (Angstrom Inc.) under an 10⁻⁸ Torr vacuum, which is integrated to the glove box. Organic layers were deposited sequentially at a rate of 0.1 Å/s and aluminum at 2 Å/s. The final device, with an active device area of 0.14 cm², was encapsulated under a nitrogen environment in the glove box using a UV curable epoxy (Epoxy Technology Inc.), and the encapsulated devices were taken outside. A Keithley 2400 source meter combined with a SpectraScan PR655 spectroradiometer (Photo Research Inc.) interfaced with a PC was used to characterize all the devices.

CONCLUSIONS

We have selected an Alq₃:C545T-based OLED as a model system to systematically study the effect of high doping concentration. It has been found that increased doping levels lead to increased excimer emission and reduced excitonic emission. As a limiting case of heavy doping, single emitter devices with C545T were fabricated with different evaporation rates. High evaporation rates alter the molecular packing of the emissive species, and thus, the red-shifted excimer emission is proven to be arising out of aggregation-induced effects. However, in both cases, that is, in a host-guest system with heavy doping and in a dopant-only single emitter device, these effects could be reversed with high electrical bias. Increased direct charge trapping and field-induced dissociation of aggregates could be the reason for this behavior. We have also fabricated dopant-only single emitter devices with different thicknesses and found that, for a device with a 70 nm thickness, the contributions from excimer and excitonic emissions are almost equal, yielding a broad emission spectrum. In this study, it has been demonstrated that the change in deposition conditions can significantly influence EL spectra, and by controlling them for the EML, OLED emission could be tuned between yellow and green by shift in emission peak and spectral broadening. Here, potential for white emission with this simple stack design can be explored by inserting a blue emitter.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03979.

Table 1. Summary of Emission Characteristics and their Dependence on Deposition Conditions and Electrical Bias for C545T-Based OLEDs

| parameters          | values          | emission characteristics |
|---------------------|-----------------|--------------------------|
|                     | low field       | high field               |
| doping concentration| 3% strong       | strong no no             |
|                     | 10% strong      | strong no no             |
|                     | 20% weak        | weak strong weak         |
|                     | 50% weak        | weak strong weak         |
| rate of deposition   | 0.1 Å/s         | strong weak no no        |
|                     | 2 Å/s           | weak strong weak         |
| thickness            | 10 nm           | weak strong strong weak  |
|                     | 20 nm           | weak strong strong weak  |
|                     | 30 nm           | weak strong strong weak  |
|                     | 60 nm           | weak strong strong weak  |
|                     | 70 nm           | weak weak strong strong  |

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Notes

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