Investigation of Förster-type energy transfer in organic light-emitting devices with 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethylylulolidin-4-yl-vinyl)-4H-pyran doped cohost emitting layer

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Organic light-emitting devices (OLEDs) with cohosted emitter, which is composed of 9,10-di(2-naphthyl)anthracene (ADN) and tris(8-hydroxy-quinolinate) aluminum (Alq3) and doped with 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethylylulolidin-4-yl-vinyl)-4H-pyran (DCJTB), were fabricated and studied. The efficiency of OLEDs with a cohost emitter was higher than that with a single host emitter. For the cohost emitter with ADN weight ratio of 75:25, the 3.4 cd/A efficiency of the resulted OLEDs was obtained. It is found that the absorption spectra of DCJTB and the emission spectra of Alq3 changed with the composition of the emitter. This phenomenon is attributed to the polarization effect. On the basis of the Förster’s theory, the resulted overlap integral exhibits the highest value for this cohost emitter. The experimental results reveal that the cascade energy transfer plays an important role in the luminance efficiency enhancement of the cohost emitter in OLEDs. © 2009 American Institute of Physics [DOI: 10.1063/1.3039412]

I. INTRODUCTION

Recently, bright and efficient organic light-emitting devices (OLEDs) have attracted wide interest due to their potential applications in flat panel display.1 To obtain bright and high efficient OLEDs, various organic materials and device structures, such as using double-layer structure,2 microcavity structure,3,4 and top-emitting architecture,5 have been reported previously. By doping two kinds of materials6,7 and applying cohosted emitter,8 high luminance emission performances of red OLEDs have been demonstrated. It has been accepted in general that Förster-type energy transfer between different dopants and/or hosts plays an important role in improving the luminescence performance. We have fully investigated the mechanism of the energy transfer process in the organic emitting layer in this study.

In this study, OLEDs with a cohosted emitter of various component ratios were fabricated and studied. The luminance efficiency of the resulted OLEDs was measured. To study the mechanisms of the observed behaviors, the energy transfer process that has taken place in the doped cohosted emitter was investigated on the basis of Förster’s theory. The spectra of the cohost mixture with various components were explored and the relationship of the spectra with the polarizability of the surrounding medium was analyzed. The parameters characterizing the energy transfer process, the spectra overlap integrals, and Förster’s radius were calculated for understanding the dependence of luminance efficiency of the resulted OLEDs on the measured composition ratio.

II. EXPERIMENTAL PROCEDURE

The cohosted emitter of OLEDs used in this study was composed by doping 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethylylulolidin-4-yl-vinyl)-4H-pyran (DCJTB) into a binary host emitter, which is a mixture of various weight ratios of 9,10-di(naphth-2-yl)anthracene (ADN) and tris(8-hydroxy-quinolinate) aluminum (Alq3). By using a vacuum thermal deposition system to deposit organic materials onto an indium-tin oxide (ITO) coated glass at a background vacuum of 2 × 10−6 Torr, the multilayer structure of OLEDs can be obtained. Figures 1(a)–1(c) show the molecular structures of ADN, Alq3, and DCJTB, the device architecture, and the energy band structure of the multilayer OLEDs,9–11 respectively. The device architecture was shown in Fig. 1(b): [Al (150 nm)−LiF (1 nm) cathode/Alq3 (5 nm)/emitting layer (30 nm)/NPB (10 nm)/m-MTDATA (40 nm)/ITO anode (150 nm)/glass]. Here Alq3 was used as the electron transporting layer, N,N′-bis(naphthalen-1-yl)-N,N′-bis(phenyl)-benzidine (NPB) as the hole transporting layer, 4,4′,4″-tris(N,3-methylphenyl-N-phenylamino)trisphenylamine (m-MTDATA) as the hole injecting layer, and LiF as the electron injecting layer.

The emitting layers of all the OLEDs are composed of 1 wt % (weight percent) DCJTB and various weight ratios (ADN:Alq3:DCJTB) of cohost materials. For simple identification, the OLEDs with various different cohost weight ratios were named as device A (ADN:Alq3:DCJTB = 100:0:1), device B (ADN:Alq3:DCJTB = 75:25:1), device C (ADN:Alq3:DCJTB = 50:50:1), device D (ADN:Alq3:DCJTB = 25:75:1), and device E (ADN:Alq3:DCJTB = 0:100:1), respectively. The luminance spectra and the Commission Internationale de l’Eclairage coordinates of the associated devices were measured with a PR650 spectrophotometer.

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To investigate the energy transfer mechanism in the co-host emitting layer of OLEDs, organic films with various co-host weight ratios were prepared. The photoluminescence (PL) spectra of the organic films with ADN:Alq3 weight ratios of 0:100, 25:75, 50:50, and 75:25 were measured using an He–Cd laser with a wavelength of 325 nm as an excitation source. The absorption spectra of the organic films with DCJTB:Alq3 weight ratios of 0:1, 1:0, 1:1, 1:10, and 1:25 were measured by an UV/visible 4100 spectrophotometer.

III. EXPERIMENTAL RESULTS AND DISCUSSION

By changing the weight ratio of ADN and Alq3 in the emitting layer of OLEDs, the difference in electrical characteristics can be observed. As shown in Fig. 2, the peak wavelength of the luminance spectrum moved toward the red side with the increase in the Alq3 weight ratio in the emitting layer, and the chromaticity coordinates of the devices were accordingly changed from (0.574, 0.403) to (0.628, 0.359). The redshift can be attributed to the polarization effect induced by environmental molecules, which is similar to the reported phenomenon that the optical characteristics of 4-(dicyanomethylene)-2-methyl-6-julolidyl-9-enyl-4H-pyran (DCM2) were changed in solvents with varying polarizabilities. It is known that ADN is a nonpolar molecule with dipole moment $\mu_{ADN} = 3.33 \times 10^{-30}$ C m and Alq3, which is a metal chelate, is a polar material with dipole moment $\mu_{Alq3} = 5.5$ D. Therefore, the polarization of the co-host emitter increases with the increase in Alq3 content in the emitter, which induces the redshift of the emission from DCJTB with the increase in Alq3 weight ratio in the co-host emitting layer.

Figure 3 shows the luminance efficiency and drive voltage at a current density of 20 mA/cm² as a function of the ADN weight ratio for 1 wt % DCJTB doped co-host emitter of OLEDs. It can be seen that the drive voltages of devices A, B, C, D, and E are 6.93, 7.97, 8.81, 9.4, and 10.13 V, respectively. The decrease in the drive voltage of the corresponding devices with increasing ADN weight ratio in the co-host mixture is attributed to the higher carrier mobility of ADN than that of Alq3.

To understand the characteristics of transport in the co-host mixture layers, we fabricated the hole-only device and used the space-charge limited conduction model to calculate the hole mobility. The hole-only device structure was Au/ADN and Alq3 mixture films/ITO/glass. The calculated hole mobilities were $3.0 \times 10^{-5}$, $9.6 \times 10^{-6}$, $5.2 \times 10^{-6}$, $2.7 \times 10^{-6}$, and $6.9 \times 10^{-7}$ cm² V⁻¹ s⁻¹ for the organic films with ADN:Alq3 weight ratios of 100:0, 75:25, 50:50, 25:75, and 0:100, respectively. The difference in hole mobility results in the enhancement of the transport performance of the co-host mixture with a higher ADN weight ratio.

As shown in Fig. 3, the luminance efficiency of the
OLEDs exhibits a composition dependent behavior in which the luminance efficiencies of devices A, B, C, D, and E with different cohost ratios are 2.4, 3.4, 2.8, 2.4, and 1.2 cd/A, respectively. The luminance efficiency of devices B, C, and D with a cohost emitter is higher than that of devices A and E with a single host emitter. The highest luminance efficiency for device B (ADN:Alq3 weight ratio of 75:25) is 3.4 cd/A. This result is similar to the previous reported one, in which a cascade energy transfer was deduced to play an important role in the luminance enhancement of the doped cohost emitter. Due to the wider ADN energy gap as compared to that of Alq3 and DCJTB, the cascade process is from ADN to Alq3 and then from Alq3 to DCJTB. But the variation in the luminance efficiency with the cohost weight ratio is still a topic of investigation. To understand the behavior, the energy transfer process that has taken place in the system was analyzed.

According to Förster’s theory, a good overlap between the emission spectra of a donor (host in our case) and the absorption spectra of the acceptor (dopant) results in a high energy transfer rate between donor and acceptor, and hence high luminance efficiency of the acceptor is obtained. When estimating Förster-type energy transfer rates from host to dopant through the spectral overlap, the emission spectra of the dopant must be separately measured under the same environment condition as the one in the practical case. We have to pay attention on it because the spectra are changed due to the polarization effect induced by the environment of different polarity, particularly the composition ratio of the cohost emitter in the case studied here. Figure 4 shows the deconvoluted absorption spectra of the organic films with DCJTB: Alq3 weight ratios of (a) 0:1 (Alq3), (b) 1:0 (DCJTB), (c) 1:1, (d) 1:10, and (e) 1:25. It can be observed that the absorption band of DCJTB shifts to a longer wavelength with the increase in the Alq3 weight ratio. As shown in Fig. 4, the peak wavelength changes from 495 nm for the film of DCJTB: Alq3 weight ratio 1:0 (pure DCJTB) to 520 nm for the film of the weight ratio 1:25. This composition dependence is attributed to the polarization effect because the Alq3 is a polar material.

FIG. 4. Deconvoluted absorption spectra of films with various DCJTB/Alq3 weight ratios.

FIG. 5. PL spectra of films with various ADN/Alq3 weight ratios.

It can be seen that the emission is mainly due to Alq3 with a single host emitter. As the weight ratio of nonpolar ADN increases, the strengthened polarization of the surrounding media makes the PL peak position of Alq3 move to a shorter wavelength from 540 nm for the film of weight ratio of 0:100 (pure Alq3) to 520 nm for the film of weight ratio of 75:25. The above composition weight ratio dependence indicates that the spectral overlap between DCJTB absorption and Alq3 emission changes with the composition weight ratio, which means that the energy transfer rate from Alq3 to DCJTB is also composition dependence.

According to the absorption spectra shown in Fig. 4, it can be found that Alq3 makes the DCJTB absorption peak shift to a longer wavelength. Figure 5 also shows that the excitiation energy transfers from ADN to Alq3, and ADN makes the Alq3 emission peak shift to a shorter wavelength. This phenomenon results in the enhanced cascade energy transfer rate from ADN to Alq3 and then from Alq3 to DCJTB. However, it is worth pointing out that the ADN emission and the Alq3 absorption are nearly independent of the environment, which can be seen from Figs. 4 and 5. It means that the energy transfer rate from ADN to Alq3 does not change with the composition weight ratio. Therefore, the composition dependence of the emission efficiency of the cohost emitter is due mainly to the energy transfer from Alq3 to DCJTB.

To understand the mechanism of the dependence of the luminance efficiency on the composition weight ratio shown in Fig. 3, the energy transfer from Alq3 to DCJTB is further analyzed. As seen from Figs. 4 and 5, the peak wavelength of the absorption band of the pure DCJTB is located at 495 nm, which is shorter than the PL peak wavelength (540 nm) of the Alq3. This phenomenon indicates that the spectral overlap between them is smaller, and hence the energy transfer from Alq3 to DCJTB would be inefficient. For a cohost emitter system, however, the situation changes owing to the polarization effect induced by coexisted molecules in the emitter. As the weight ratio of nonpolar ADN increases, the polarization of the surrounding media is weakened, which makes the PL peak position of Alq3 move to a shorter wavelength. Similarly, the strengthened polarization of the surrounding media makes a redshift of the absorption peak of DCJTB as the weight ratio of Alq3 increases. These changes...
result in the increase in the spectra overlap and Förster radius. The Förster radius can be expressed as follows:  
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R_0^2 = \frac{0.5291 \beta^2}{N_A n^4} \int_0^\infty f_D(v)e_A(v) \frac{dv}{v^2},
\]
where \(v\) is the wave number, \(e_A(v)\) is the molar extinction coefficient, \(f_D(v)\) is the normalized spectral distribution of fluorescence, \(\beta^2\) is an orientation factor (2/3 for random orientation), \(N_A\) is the Avogadro’s number, and \(n\) is the refractive index of the host.

To calculate the overlap integral, we use the PL spectra of Alq3 in the organic films with various ADN:Alq3 weight ratios shown in Fig. 5 and the absorption spectra of DCJTB shown in Fig. 4. It is noted from Fig. 4 that the absorption band of DCJTB was located nearly at the same position for all the cohost emitters of devices B, C, D, and E, in which the composition weight ratios of DCJTB:Alq3 were smaller than 1:25. The calculated overlap integrals for emitters with ADN:Alq3 weight ratios of 75:25, 50:50, 25:75, and 0:100 were 1.21 × 10^{-14}, 1.14 × 10^{-14}, 1.05 × 10^{-14}, and 0.97 × 10^{-14} 1 cm^3 mol^{-1}, respectively. For device A, the overlap integral of 0.91 × 10^{-14} 1 cm^3 mol^{-1} was obtained. Taking a refractive index of 1.7 for both Alq3 and ADN as well as their mixture, we accordingly obtained the Förster radius of 29.34, 30.45, 30.14, 29.73, and 29.66 Å for devices A, B, C, D, and E, respectively. The results calculated above indicate that the overlap integral value and Förster radius for device B with a cohost weight ratio of 75:25 (ADN:Alq3) are larger than those for all other devices. This fact implies that the device B reveals the highest luminance efficiency, which is consistent with the experimental results shown in Fig. 3. The cohost weight ratio dependences of both overlap integral and luminance efficiency also reveal a similar tendency. The above results provide further evidence to the observation that the cascade energy transfer process plays an important role in the luminance performance improvement of OLEDs with cohost emitter.

IV. CONCLUSIONS

OLEDs with DCJTB doped ADN/Alq3 cohost emitter were fabricated and the regularity of their luminance efficiency variation with ADN/Alq3 composition weight ratio was investigated. It was found that device B with ADN/Alq3 cohost weight ratio of 75:25 exhibited the highest luminance efficiency of 3.4 cd/A. To understand this composition dependence, the influences of the polarization effect on the spectra of the host and the dopant in films of different composition ratios were studied. The Förster’s overlap integrals were then calculated by using the measured spectra. Based on the analyses of the overlap integrals, it is concluded that the energy transfer efficiency between Alq3 and DCJTB changes with the composition of the emitter and shows a similar dependence on the ADN/Alq3 weight ratio in the cohost emitter. Especially the overlap integral for ADN/Alq3 weight ratio of 75:25 exhibits the highest one, which is consistent with the experimental result that device B has the highest luminance efficiency. This phenomenon indicates that the polarization effect has to be considered in analyzing the energy transfer process in OLEDs. The results obtained in this work provide further evidence to the observation that the cascade energy transfer process plays an important role in the luminance performance improvement of OLEDs with cohost emitter.

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