Observation of dynamic energy transfer and quenching in doped tris(8-hydroxyquinoline) aluminum thin films with time-resolved photoluminescence spectroscopy

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Photoluminescence (PL) and time-resolved photoluminescence (TRPL) of the organic films that are composed of tris(8-hydroxyquinoline) aluminum (Alq_3) as the host and 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H, 5H,11H,[l]benzopyrano[6,7,8-ij]quinolizin-11-one (C545T) as the green dopant of different concentrations are measured. In TRPL measurements, we observe that the carrier lifetime decreases monotonically with increasing doping concentration. It may result from the more efficient energy transfer from the host to dopant and/or the higher absorption due to the concentration dependent quenching behaviors in the Alq_3/C545T system. The time constant for energy transfer from the host to the dopant decreases with increasing doping concentration. However, it saturates when the doping concentration is higher than 2%. That means (1) the higher doping concentration has little contribution for C545T emission which is consistent with the steady state PL results, and (2) optical absorption plays an important role when the doping concentration exceeds 2%.

1. Introduction

Organic light-emitting devices (OLEDs) have attracted much attention because they exhibits the advantages of low-power consumption, high brightness, high contrast, and low cost [1,2]. In such a device, doping high internal-quantum-efficiency (IQE) material in the charge transport organic to form a light-emitting layer (EML) can effectively increase the output spectral range and the device lifetime [3]. It can also reduce the unwanted self-absorption [4,5]. However, when the doping concentration increases, the excited dopants will form excimers or aggregates that generally causer the effect of concentration quenching [6,7]. Once the excitation energy is trapped in an aggregate, it may return to the ground state, either through light emission with a wavelength different from that of the excitons or through nonradiative relaxation. In such a host-dopant material system, the Förster energy transfer dominates the whole relaxation process [8]. This transfer process involves a long-range dipole-dipole coupling, which results in the transfer of the excited-state energy from a host donor to a guest acceptor. To implement the singlet exciton transfer from the host through the Förster transfer process, the energy level of the singlet in the host has to lie above the corresponding level in the guest. Also, efficient transfer requires an overlap of emission in the host and absorption in the guest.

With increasing concentration of the guest acceptor, efficient energy transfer is expected to be achieved. However, a higher guest acceptor concentration also results in the concentration quench effect. Typically, the energy transfer and concentration quench are two of the most important issuer in the carrier dynamics of OLED materials [9,10]. They play crucial roles in OLED device design for achieving high efficiency [11] and long lifetime [12]. In this paper, we study the energy transfer process in the organic thin films. The thin films are composed of tris(8-hydroxyquinoline) aluminum (Alq_3) as the host material and 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H,[l]benzopyrano[6,7,8-ij]quinolizin-11-one (C545T) as the green guest material of different concentrations. We observe three interesting phenomena with the time-resolved photoluminescence (TPPL) technique [13] in such thin films: (1) the energy transfer time decreases from 1.4 ns to about 400 ps in increasing doping concentration from 1 to 2 %. However, the decreasing trend of the energy transfer time saturates when the doping concentration is further increased to 5%. (2) Carrier lifetime decreases monotonically with increasing doping concentration due to the increase of nonradiative recombination rate.

2. Experimental results and discussions

In our experiments, thin organic films of 50 nm in thickness were deposited on the glass substrate with a ULVAC multi-chamber vacuum evaporator. Prior to the deposition, the surface of glass was cleaned with O_2 plasma to remove impurities. Five samples were fabricated with different doping concentrations, i.e., 0, 1, 2, 4 and 5

%, which are labeled as samples A, B, C, D, and E, respectively. Photoluminescence (PL) measurement was carried out at room temperature with a 325 nm line He-Cd laser. TRPL measurement was performed by using a Hamamatsu streak camera (Hamamatsu Photonics KK, Japan) in conjunction with a 25 cm monochromator. The excitation beam at 400 nm came from the second-harmonic generation of a mode-locked Ti:sapphire laser with a pulse width of 100 fs and a repetition period of 13.16 ns.

PL spectra of various samples are shown in Fig. 1. With increasing doping concentration, first, PL intensity increases and spectral peak red-shifts because energy transfer from host to dopant is more efficient. Maximum PL intensity is achieved at 2% doping concentration of sample C. When doping concentration is over 2%, decreasing PL intensity shows a clear concentration quenching effect. This result is consistent with what reported [14]. The inset of Fig. 1 shows the peak wavelength variation with the doping concentration. The spectral peak shifts from 521.5 to 527 nm within the considered doping concentration range. These two wavelengths, corresponding to the emission peaks of Alq_3 and C545T, respectively, will be used as the probe spectral positions in the following measurements.
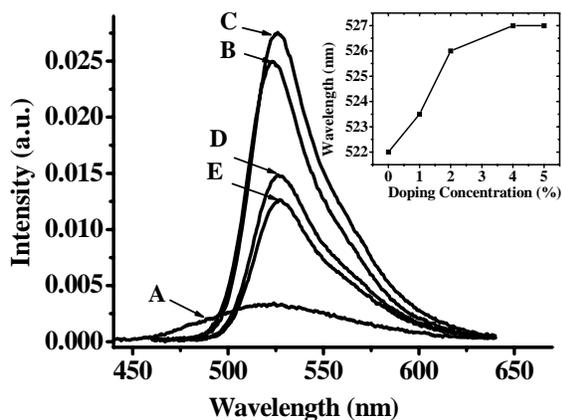
Fig. 1. PL spectra of the samples of different doping concentrations ranging from 0 to 5 %. The inset plows the variation of the spectral peak positions with doping concentration.

Figs. 2(a) and (b) show the time-dependent intensity decay at the wavelengths of 521.5 and 527nm, respectively. The decay time constants in Fig. 2(a) are calibrated to be 15.4, 1.542, 0.787, 0.444 and 0.317 ns, with increasing doping concentrations, respectively. The corresponding values in Fig. 2(b) are 9.612, 1.673, 0.862, 0.497 and 0.431 ns, indicating another decreasing trend with increase doping concentration. For a certain doping concentration, the decay time constant at the dopant probe wavelength (527 nm) is larger than that at the host probe wavelength (521.5 nm) except in the undoped condition (sample A). This result clearly reflects the behavior of energy transfer from the host to dopant material. As the doping

concentration increases, the decay time constant decreases that can be attributed to the higher energy transfer probability. Another possible mechanism for the decreasing trend is the absorption originating from the concentration quenching effect. Typically, the model of quasi-planar molecular packing induced dye-dye interaction is used for explaining such a phenomenon. However, it is still difficult to separate the effects of energy transfer and optical absorption with such an analysis. Besides, the spectral overlap between Alq_3 and C545T makes the identification of either effect more difficult.
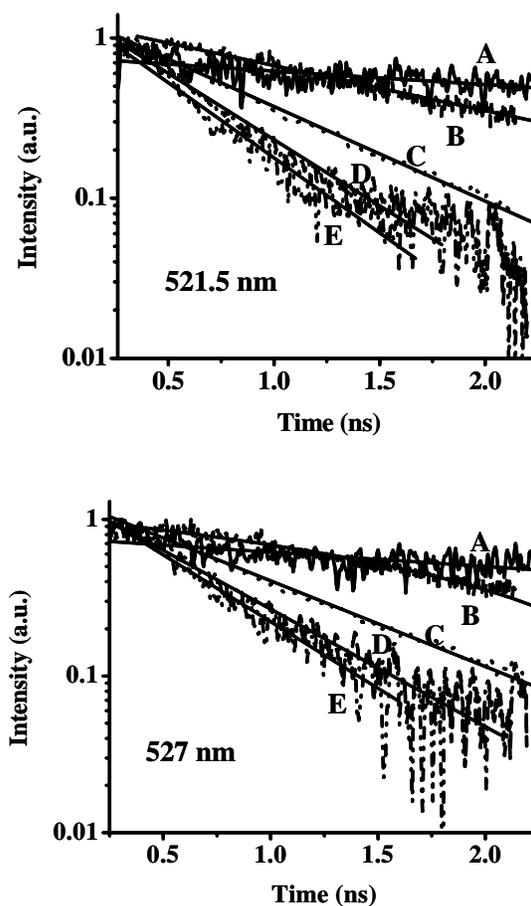
Fig. 2. Time-dependent PL intensity profiles at (a) 521.5 and (b) 527 nm, with different doping concentrations.

Fig. 3 shows the spectra of sample C taken with temporal solution. One can observe that the peak position red shifts with increasing time from 68.75 to 1306.25 ps. By monitoring the relative intensities at the host and dopant probe wavelengths at different temporal positions, we can define the energy transfer time with the intensities at 521.5 and 527 nm being equal. The energy transfer time is plotted for different samples in Fig. 4. In increasing doping concentration, the energy transfer time decreases rapidly and then saturates at high concentrations. Such a

behavior is related to the fact the Förster energy transfer is a long-range process. The long transfer time is due to the weak interaction of low doping concentration. As doping concentration increases, the physical distance for Förster energy transfer between the host and guest materials decreases and hence the transfer time decreases.
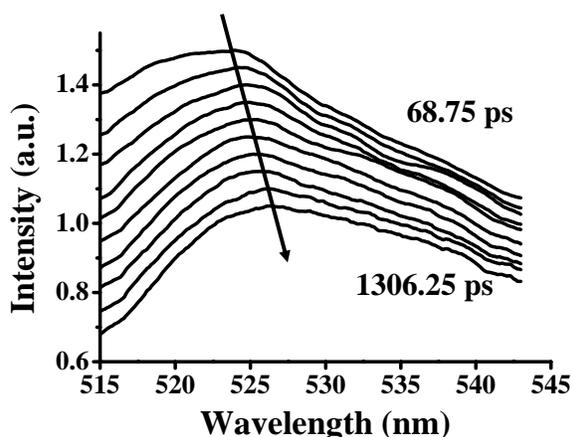
Fig. 3. Spectral evolution of sample C.
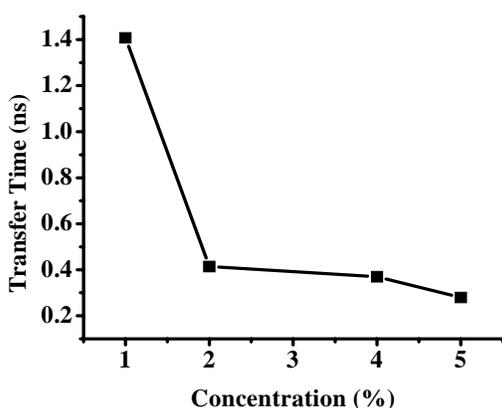
Fig. 4. Energy transfer times of samples B, C, D and E.

Hence, we may deduce that the monotonically decreasing carrier lifetime with increasing doping concentration, as shown in Figs. 2(a) and (b), indicates that optical absorption does play a certain role at higher doping levels, over 2%, originating from the concentration quenching effect. This absorption may come from the aggregate absorption or excimer energy relaxation of the spectrum.

3. Conclusions

In summary, we have reported the cw and time-resolved PL behaviors of the organic thin films which composed of the host emitting material Alq_3 and the doping material C545T with different doping concentrations. The doping concentration had an optimized value at 2% for the maximum PL efficiency. From the TRPL measurements, we observe the energy transfer rate increases with increasing doping concentration and saturates at about 2% which is consistent with the PL measurements. On the other hand, nonradiative recombination rate increases with increasing doping concentrations monotonically which may comes from the aggregate absorption or excimer energy relaxation.

References

[1] M. A. Baldo, M. E. Thompson, S. R. Forrest, Nature (London) **403**, 750 (2000).
[2] X. Gong, M. R. Robinson, J. C. Ostrowski, D. Moses, G. C. Bazan, A. J. Heeger, Adv. Mater. **14**, 581 (2002).
[3] X. Gong, J. C. Ostrowski, G.C. Bazan, D. Moses, A. J. Heeger, Appl. Phys. Lett. **81**, 3711 (2002).
[4] R. A. Negres, X. Gong, J. C. Ostrowski, G. C. Bazan, D. Moses, A. J. Heeger, Phys. Rev. B **68**, 115209 (2003).
[5] J. Kalinowski, W. Stampor, M. Cocchi, D. Virgili, V. Fattori, P. Di Marco, Chem. Phys. **297**, 39 (2004).
[6] R. N. Bera, Y. Sakakibara, M. Tokumoto, K. Yase, J. J. Appl. Phys. **42**, 7379 (2003).
[7] D. R. Lutz, K. A. Nelson, C. R. Gochanour, M. D. Fayer, Chem. Phys. **58**, 325 (1981).
[8] M. A. Baldo, S. R. Forrest, Phys. Rev. B, **62** 10967 (2000).
[9] D. Vacar, E. S. Maniloff, D. W. McBranch, A. J. Heeger, Phys. Rev. B **56**, 4573 (1997).
[10] G. Cerullo, S. Stagira, M. Zavelani-Rossi, S. D. Silvestri, T. Virgili, D. G. Lidzey, D. D. C. Bradley, Chem. Phys. Lett. **335**, 27 (2001).
[11] Z. Zhang, Q. Wang, Y. Dai, Y. Liu, L. Wang, D. Ma, Org. Electron. **10**, 491 (2009).
[12] J. H. Lee, J. J. Huang, C. C. Liao, P. J. Hu, Y. Chang, Chem. Phys. Lett. **402**, 335 (2005).
[13] R. Reisfeld, E. Zigansky, E. Vaganova, S. Yitzchaik, Opt. Mater. **30**, 1710 (2008).
[14] L. S. Hung, C. H. Chen, Mater. Sci. Eng. R-Rep **39**, 143 (2002).

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