

## *In situ* photoluminescence investigation of doped Alq

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We report the photoluminescence (PL) properties measured *in situ* from vacuum-deposited organic films of tris-(8-hydroxyquinoline) aluminum (Alq) doped with 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM), where the red emission from the guest molecules is due to Förster energy transfer of excited state energy from host to guest. Both bare DCM-doped Alq (Alq:DCM) and bilayer Alq/Alq:DCM films have been studied, with the thickness of the Alq overlayer continuously varied in the latter case. The PL spectra from the bilayer structure contain no Alq contribution when its thickness is below 2.4 nm. Taking the value as the maximum distance for which the Alq exciton can travel in the film and still transfer its energy to a DCM molecule, the minimum DCM concentration in Alq:DCM necessary to produce red emission only can be estimated at 0.31 wt %. The most efficient red emission appears at the DCM concentration of about 1.7 wt %, at which more than 90% Alq-originated excitons are involved in the Förster energy transfer process. There exists a gradual red shift of the PL spectra with increasing DCM concentration, which can be attributed to the polarization and accompanying aggregation tendency of DCM molecules in Alq during the formation of the doped films. © 2002 American Institute of Physics.

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Organic light-emitting devices (OLEDs) are among the most attractive candidates for full-color, flat-panel displays. Besides its high brightness and efficiency, an OLED is easily tuned to emit at different wavelengths by incorporating proper dyes into the organic host of emitter. 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) is one of the most commonly used dyes for red emission and hence receives intensive investigation for its potential applications in red-emitting OLEDs and organic semiconductor lasers.<sup>1–11</sup> It was recently reported that for a DCM-doped tris-(8-hydroxyquinoline) aluminum (Alq:DCM) film, emission could be tuned from green, peaked at wavelength of 530 nm, to red, peaked at 625 nm, simply by increasing the DCM concentration from zero to 5%.<sup>2</sup> In such a system, energy may transfer from photo- or electro-excited Alq molecules to DCM molecules via exciton diffusion, giving rise to enhanced red emission, as is described by Förster's energy transfer model.<sup>1,3,4,12,13</sup> Obviously, here the number of the DCM molecules available in the transfer process plays a crucial role: on one hand, a low DCM concentration may lead to insufficient red emission due to lack of the red emitters; on the other hand, however, a too high doping concentration may lead to exciton quench and red-shift of the emission spectrum. To acquire the optimum doping concentration, one needs to determine the maxi-

imum distance that the Förster energy transfer may dominate. In this letter, we present an *in situ* photoluminescence (PL) investigation on Alq-covered Alq:DCM films with the thickness of the Alq overlayer changing from zero to tens of nanometers. It turns out that the distance available for efficient energy transfer, or "capture radius" of a DCM molecule, is 2.4 nm. It is also estimated that the lowest DCM concentration needed for pure red emission resulting only from recombination of DCM-originated excitons is 0.31 wt %, and that the most efficient red emission appears at the DCM concentration of about 1.7 wt %, at which more than 90% Alq-originated excitons are involved in the Förster energy transfer process.

Same as in device fabrications, indium-tin-oxide-coated glass plates were used as substrates in the present experiments. Prior to preparation of the organic bilayer structure, the substrate was ultrasonically cleaned in acetone, ethanol, and deionized water sequentially, 5 min each. Then, a 70-nm-thick layer of Alq:DCM (1.4 wt %, featured by pure red emission) was vacuum co-evaporated onto the clean substrate, at base pressure of  $2 \times 10^{-5}$  Pa. Finally, a homogeneous pure Alq layer was deposited on the top of the Alq:DCM layer,<sup>14</sup> during which PL spectra were measured, as schematically shown in Fig. 1. A PC1000 spectrometer of Ocean Optic Inc. combined with a He-Cd laser ( $\lambda = 441.6$  nm) were used to take the PL measurements, with the inward pumping beam and the outward emitting light traveling through two separate viewports of the deposition

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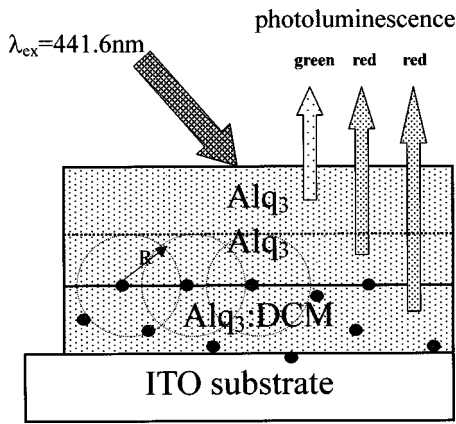


FIG. 1. Configuration of the *in situ* prepared Alq/Alq:DCM specimen.

chamber. The whole process of the *in situ* measurements was computer-controlled, with the thickness of the growing Alq film monitored by a quartz crystal rate/thickness monitor (Sigma SQM 160). To ensure accuracy of the data measured, crosscheck of the film thickness was done by means of scanning electron microscopy.

Figure 2(a) shows the PL spectra measured at various Alq thicknesses, ranging from 0 to 15 nm. The starting spectrum of the Alq:DCM film is featured by a somewhat broadened peak centered at around 610 nm, with full width at half maximum of 87 nm. The spectra remain unchanged for the Alq thicknesses up to about 2.4 nm. After that, there emerges another peak at about 525 nm, whose intensity increases linearly with the increasing Alq thickness, as shown in Fig. 2(b). We thus assume 2.4 nm the maximum distance over which energy transfer between an Alq molecule and a DCM molecule dominates so that the 525 nm green emission from the Alq molecule can be suppressed. The radius *R* in Fig. 1 represents such a captive distance. For the Alq molecules within the *R*-circle, energy transfer towards the DCM mol-

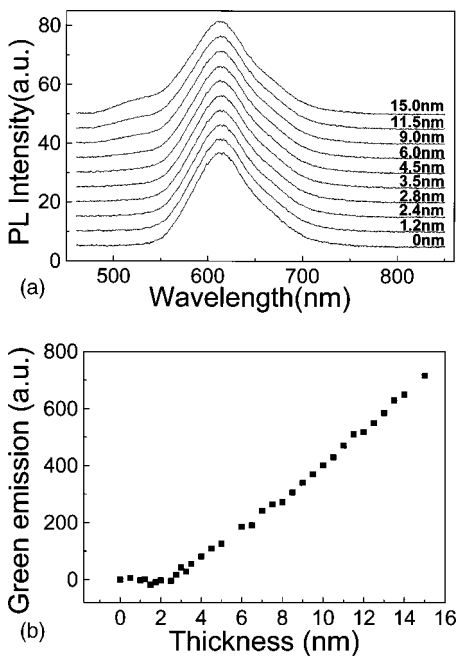


FIG. 2. PL spectra taken from the Alq/Alq:DCM specimen with different thicknesses of the Alq overlayer (a) and dependence of the intensity of the green emission on the Alq thickness in Alq/Alq:DCM (b).

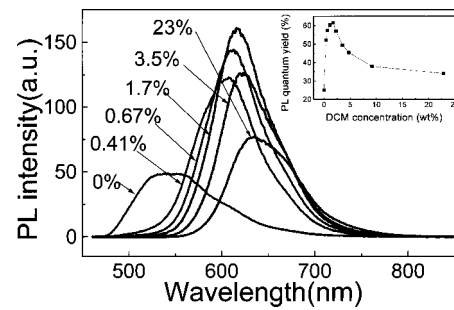


FIG. 3. PL spectra taken from bare Alq:DCM films with different DCM concentrations. The *QY* values of the films with the inset.

ecule in the center may prevail over intrinsic emission of the green light.

The reported value of Alq's density is 1.51 g/cm<sup>3</sup>.<sup>15</sup> Thus, given the molar mass, 459 g, the average volume an Alq molecule occupies in an amorphous film can be estimated as a cube of 0.8-nm-long sides. So the capture radius of DCM measured in the present work is three times as large as the nearest molecular spacing of Alq on average. That means the lowest concentration needed for pure red emission from an Alq:DCM system is one DCM molecule in (2 × 3)<sup>3</sup> Alq molecules, namely, 0.46 mol %, or 0.31 wt % (molar mass of DCM is 303 g).

More efficient red emission is available at higher DCM concentrations, accompanied by red-shifted wavelengths. Figure 3 shows such a dependence of the PL intensity on the DCM concentration. Here the spectra were taken from bare Alq:DCM films, with their intensities normalized to that of a referential Alq film prepared on the same substrate each time. Shown in the inset are the values of the quantum yield (*QY*) of these composite films estimated from their PL intensities, by taking 25% as the *QY* value of the pure Alq film.<sup>16,17</sup> The highest *QY* value so derived is 61%, attainable at the DCM concentration of around 1.7 wt %, or 2.6 mol %. Further increase in the DCM concentration results in a gradual decrease in the *QY* value. In other words, if more than one DCM molecule is present in about 40 Alq molecules on average, exciton quench is likely to occur so that not all of the Alq-originated excitons can contribute to the red emission. Given 0.8 nm as the average molecular spacing and 40 the average number of the Alq molecules in a DCM-centered cube, one can roughly estimate that the largest separation *r*<sub>max</sub> between the DCM molecule and an Alq molecule in the corner is about 2 nm, one tenth of the diffusion length *ℓ* of an exciton in Alq.<sup>1</sup> That means even the excitons originating from the farthest Alq molecules in the cube may still have the probability of 90% to reach where the DCM molecule is located. Thus, the average probability for the Alq-originated excitons to meet the DCM molecule can be estimated at

$$\frac{\int_0^{r_{\max}} 4\pi r^2 e^{-r/\ell} dr}{\int_0^{r_{\max}} 4\pi r^2 dr} = \frac{3}{r_{\max}^3} \int_0^{r_{\max}} r^2 e^{-r/\ell} dr = 93\%.$$

Since the lifetime of DCM-originated excitons is much shorter than that of Alq-originated, it is reasonable to assume that all the Alq-originated excitons reaching the DCM molecule will transfer energy to it. That is to say, in the most

efficient case, as many as 93% Alq-originated excitons are probably involved in the Förster energy transfer process.

Red shift observed in the present experiments can be attributed to polarization of DCM molecules and accompanying aggregation tendency, as is reported by many researchers.<sup>18–22</sup> Such a phenomenon is present not only in a pure DCM film, but also in Alq:DCM films. In the latter case, as the DCM concentration is increased, the possibility for two DCM molecules to get together also increases, which leads to enhanced emission at longer wavelengths. Thus occurs the red shift. If too many molecules get together, however, the emission would be smeared due to concentration quench.

In conclusion, we have *in situ* investigated the PL behavior of DCM-doped Alq films. By applying Förster's energy transfer model to the bilayer structure of Alq/Alq:DCM, it is found that a DCM molecule can efficiently capture excitons originating from the Alq molecules within a radius of a few nanometers only. Based on this result, the lowest doping concentration needed for pure red emission has been estimated to be 0.31 wt %. Furthermore, the PL intensity versus the DCM concentration measured from bare Alq:DCM films show that, at optimized doping, more than 90% Alq-originated excitons are involved in the Förster's energy transfer process, giving rise to highly efficient red emission.

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- <sup>1</sup>C. W. Tang, S. A. VanSlykex, and C. H. Chen, *J. Appl. Phys.* **65**, 3610 (1989).
- <sup>2</sup>A. Böhrer, P. Urbach, J. Schöbel, S. Dirr, H.-H. Johannes, and S. Wiese, *Physica E (Amsterdam)* **2**, 562 (1998).
- <sup>3</sup>T. Mori and T. Mizutani, *Polym. Adv. Technol.* **8**, 471 (1997).
- <sup>4</sup>T. Mori, K. Obata, and T. Mizutani, *J. Phys. D* **32**, 1198 (1999).
- <sup>5</sup>V. Bulovic, V. G. Kozlov, V. B. Khalfin, and S. R. Forrest, *Science* **279**, 553 (1998).
- <sup>6</sup>X. T. Tao, S. Miyata, H. Sasabe, G. J. Zhang, T. Wada, and M. H. Jiang, *Appl. Phys. Lett.* **78**, 279 (2001).
- <sup>7</sup>F. Hide, M. A. Díaz-García, B. J. Schwartz, M. R. Andersson, Q. Pei, and A. J. Heeger, *Science* **273**, 1833 (1996).
- <sup>8</sup>V. G. Kozlov, V. Bulovic, and S. R. Forrest, *Appl. Phys. Lett.* **71**, 2575 (1997).
- <sup>9</sup>V. G. Kozlov, V. Bulovic, P. E. Burrows, M. Baldo, V. B. Khalfin, G. Parthasarathy, S. R. Forrest, Y. You, and M. E. Thompson, *J. Appl. Phys.* **84**, 4096 (1998).
- <sup>10</sup>M. Berggren and A. Dodabalapur, *Appl. Phys. Lett.* **72**, 410 (1998).
- <sup>11</sup>S. R. Forrest, *Chem. Rev.* **97**, 1793 (1997).
- <sup>12</sup>M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals*, (Oxford, New York, 1982).
- <sup>13</sup>M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature (London)* **395**, 151 (1998).
- <sup>14</sup>S. Tokito, J. Sakata, and Y. Taga, *Appl. Phys. Lett.* **64**, 1353 (1994).
- <sup>15</sup>C. H. M. Marée, R. A. Weller, L. C. Feldman, K. Pakbaz, and H. W. H. Lee, *J. Appl. Phys.* **84**, 4013 (1998).
- <sup>16</sup>N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. A. R. R. Kessener, S. C. Moratti, A. B. Holmes, and R. H. Friend, *Chem. Phys. Lett.* **241**, 89 (1995).
- <sup>17</sup>H. Mattoussi, H. Murata, C. D. Merritt, Y. Lizumi, J. Kido, and Z. H. Kafafi, *J. Appl. Phys.* **86**, 2642 (1999).
- <sup>18</sup>K. Yoshino, A. Fujii, H. Nakayama, S. Lee, A. Naka, and M. Ishikawa, *J. Appl. Phys.* **85**, 414 (1999).
- <sup>19</sup>K. Yase, Y. Yoshida, S.-S. Sumimoto, N. Tanigaki, H. Matsuda, and M. Kato, *Thin Solid Films* **273**, 218 (1996).
- <sup>20</sup>S. Goncalves-Conto, M. Carrard, L. Si-Ahmed, and L. Zuppiroli, *Adv. Mater.* **11**, 112 (1999).
- <sup>21</sup>E.-M. Han, L.-M. Do, and M. Fujihira, *J. Appl. Phys.* **80**, 3297 (1996).
- <sup>22</sup>K.-H. Weinfurter, H. Fujikawa, S. Tokito, and Y. Taga, *Appl. Phys. Lett.* **76**, 2502 (2000).