

## Aggregation and permeation of 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran molecules in Alq

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The morphologic and luminescent behaviors of various 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) containing films have been investigated. This involves pure DCM layers deposited on top of a tris-(8-hydroxyquinoline) aluminum (Alq) layer or positioned between two Alq layer, DCM-doped Alq films, and periodically arranged Alq/DCM multilayer structures. The occurrence over a period of time of aggregation and permeation of DCM molecules at room temperature and at temperatures as low as  $\sim 260$  K is found in all the cases studied. Such a phenomenon will result in degradation of related organic light-emitting devices and is closely related to the electric polarity of the DCM molecule. © 2002 American Institute of Physics. [DOI: 10.1063/1.1497438]

One of the important topics currently of interest for organic light-emitting device (OLED) researchers is the realization of stable operation of high-efficiency red emitters. A laser dye, 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM), is one of the most commonly used red emitters in color OLEDs and has been intensely researched.<sup>1–14</sup> This is especially the case for DCM-doped tris-(8-hydroxyquinoline) aluminum, Alq (Alq:DCM). Both the color and efficiency of the emission are heavily dependent on the doping concentration of DCM, as was discussed in detail by many researchers.<sup>1–3,15,16</sup> It was found that the degradation of OLEDs was related to intermolecule aggregation of quinacridone and formation of dimers or oligomers,<sup>15</sup> which might be undesirable for electroluminescence (EL). But a clear and affirmable explanation for the key mechanism of degradation of the OLEDs with doped film(s) is not available so far.

In this letter, we present an investigation of the migration of DCM molecules in Alq and suggest that the migration-accompanying aggregation and permeation of the DCM molecules in Alq is one of the key mechanisms of degradation of the related OLEDs. It has been found that the aggregation and permeation can take place not only at room temperature, but also at temperatures as low as about 260 K. The phenomena may occur not only during operation, but also during storage of the devices. A possible underlying mechanism of the phenomena has also been proposed.

The Alq and DCM specimens used in the present experiments were prepared by means of vacuum deposition on cleaned Si wafers or on indium-tin-oxide (ITO)-coated glass

plates. During the deposition, the pressure in the chamber was kept at  $2 \times 10^{-5}$  Pa, and the thickness of the film was monitored with a quartz oscillator thickness/rate monitor and was accurately controlled. The deposited specimens were marked luminescently through photoluminescence (PL), pumped with a He–Cd laser of wavelength 441.6 nm. Their morphologies were observed by both optic microscopy and scanning electronic microscopy (SEM). Three kinds of specimen with different structures were prepared and measured, as detailed below.

Specimen I was prepared on a cleaned Si wafer substrate. First, a 100-nm-thick Alq film was deposited, and then, a 73-nm-thick DCM film was deposited on this Alq film. Second, with the specimen half shaded by a shutter, another layer of Alq was deposited. Its thickness was 30 nm. After the deposition, optic microscopic and SEM observations were made for the two different halves and then the specimen was stored in a dry chamber until another SEM observation one month later.

Specimen II, again on a Si substrate, was a 50-nm-thick Alq:DCM film with a DCM concentration of 0.28 wt%. The specimen was prepared for a series of PL measurements, ranging from almost immediately after the preparation to up to about 174 h later.

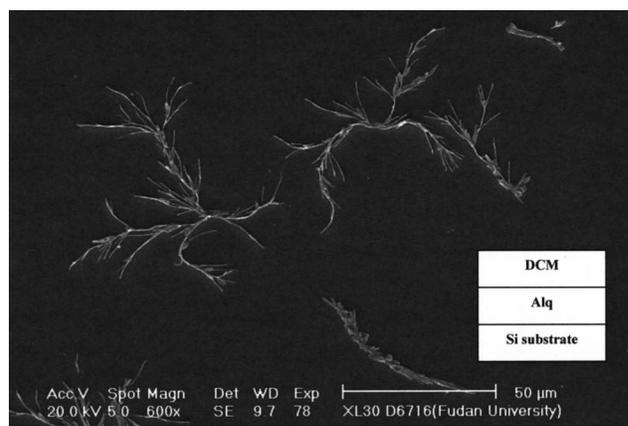
Specimen III consisted of ten layers of 7-nm-thick Alq films and ten layers of 1-nm-thick DCM films alternately deposited on a cleaned ITO-coated glass substrate. The top layer was a DCM film and the bottom layer adjacent to the ITO substrate was an Alq film. PL measurements of the specimen were also made at different time after it was prepared.

Upon the sequential deposition of Alq (100 nm), DCM

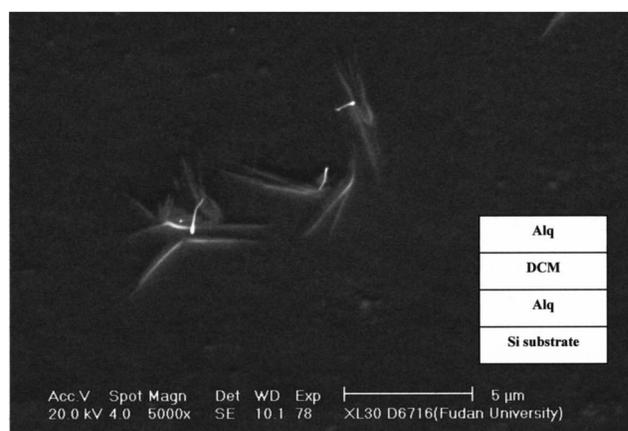
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(73 nm) and Alq (30 nm) films, the surfaces of the two halves of specimen I were homogeneous and smooth, as observed by a microscope and a SEM, consistent with what was previously reported for organic thin films.<sup>4</sup> After being stored for one month, however, the two surfaces exhibited different morphologies. Figure 1(a) shows the SEM image taken from the DCM-terminated half of the specimen I. As one can clearly see, the surface is no longer homogeneous but characterized by a branch-shaped pattern. This obviously results from molecular aggregation, showing that the DCM molecules have migrated and aggregated on the Alq film. Similarly, the DCM film sandwiched between the two Alq layers also tends to aggregate, as shown in Fig. 1(b). The hypothesis is that the featured SEM pattern results not from the outermost Alq layers but from the sandwiched DCM film, and is based on the fact that a pure Alq film does not show any tendency to aggregate, as will be further discussed below.

As shown above, since DCM molecules may aggregate either in outermost layers or when sandwiched between two Alq films, it is then interesting to examine whether the DCM molecules will aggregate when they are used as dopant in Alq matrix. The latter case is actually even more important, considering DCM always acts as a dopant, not a host material, in the red-emitting OLEDs. But the low DCM concentration (less than 1 wt% usually) in a high-efficiency red-emitting Alq:DCM film makes the morphologic variation too insignificant to observe. Alternatively, PL measurements can help solve the problem in such a case, as aggregated molecules should show different PL behaviors than dispersive ones.<sup>1</sup> This is exactly what one may find from the variation of the PL spectra taken from specimen II shown in Fig. 2. Here the five spectra were acquired at 0, 6, 12, 72 and 174 h after the deposition of the Alq:DCM film, as labeled. Two features are immediately evident. First, the intensity of the red emission at around 600 nm reduced gradually after preparation of the specimen; and second, the green emission at about 530 nm grew monotonically. These two processes create a blueshift. Obviously, the enhancement in the green emission is due to the lessening of the dispersion of the DCM dopants in the Alq film, which results from the DCM aggregation. Thereafter, degrading of the doped film dominates, giving rise to a more Alq-like PL behavior. Similar phenomena have also been observed in the electroluminescence (EL) of our OLEDs with Alq:DCM films as the emitter. In those cases, degradation occurs with the appearance of some black spots on the device surface or even before the formation of the black spots. This means that even at very low DCM concentrations (0.28 wt% in this case), DCM molecules in the Alq:DCM film still tend to aggregate. Local concentrations of the aggregated DCM molecules lead to a quenching of emission in the region of concentration, and less of the DCM molecules join in the energy transfer, activation and emission processes. As a result, the red emission reduces and the green emission increases. It is unlikely that the aggregation could be simply ascribed to the Joule heating effect, as suggested by Mori.<sup>16</sup> Actually, we have observed that the aggregation of DCM molecules in Alq occurs not only at room temperature, but also at considerably lower temperatures ( $\sim 260$  K). We also find that the EL character-



(a)



(b)

FIG. 1. SEM images of (a) a 73-nm-thick DCM layer deposited on a 100-nm-thick Alq layer and (b) another 30-nm-thick Alq layer on (a). Both spectra were measured one month after the preparation of the specimens. The insets show the corresponding structures.

istics of our OLEDs, with Alq:DCM films as the emitter, exhibit similar degradation after being stored for a long time without any operation. This further confirms that the current-induced Joule heating in an EL device is not the cause of aggregation, but only accelerates the aggregation.

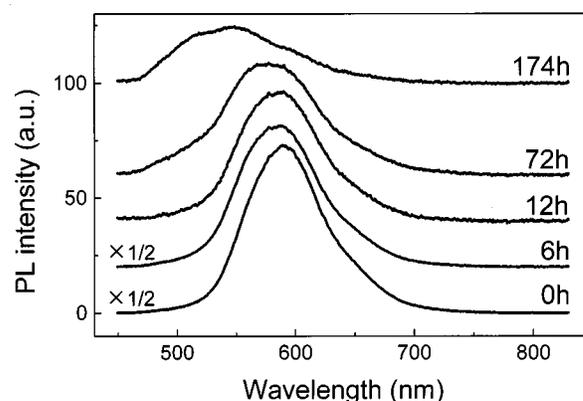


FIG. 2. PL spectra of the Alq:DCM film with a DCM concentration of 0.28 wt%. The five spectra were measured at 0, 6, 12, 72, and 174 h after the preparation of the specimen as labeled.

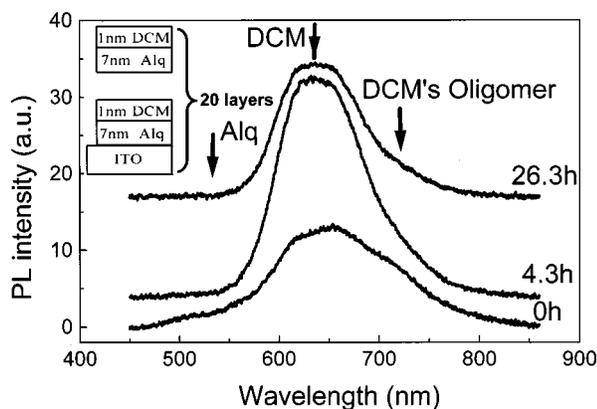


FIG. 3. PL spectra of a DCM-Alq multilayer specimen with its structure shown in the inset. The three spectra were measured at 0, 4.3 and 26.3 h after the preparation of the specimen as labeled.

In addition to aggregating by themselves, DCM molecules can permeate into the Alq layers. Figure 3 shows the PL spectra of specimen III measured at 0, 4.3 and 26.3 h after preparation. One can see that the spectrum measured from the as-prepared specimen (labeled “0h”) contains not only the red emission from DCM, peaked at about 630 nm, but also the green emission from Alq, peaked at about 530 nm. After 4.3 h, however, with the red emission enhanced significantly, the green emission becomes too weak to observe. These phenomena can be ascribed to the migration of the DCM molecules across the DCM-Alq interfaces, which are relatively sharp when they have just been prepared. That is to say, initially, the Alq molecules located near the middle of the Alq layers are too far from the DCM molecules to transfer photon-induced energies and can only radiate by themselves.<sup>17</sup> Migration of the DCM and Alq molecules results in permeation of some DCM molecules deeply into the Alq layers, and vice versa. Thus all the Alq-originated excitons can have a high probability to approach, and thus transfer energy to the adjacent DCM molecules, leading to enhancement of the red emission from DCM and even to annihilation of the green emission from Alq. Besides the peak at about 630 nm, there exists a discernable shoulder between 700 and 750 nm in all three spectra shown in the figure. The intensity of this shoulder decreased slowly with time. This can be ascribed to the existence of DCM aggregates, like dimers or oligomers, which result from bound molecules.<sup>18–22</sup> The slowly decreasing shoulder, together with the decrease of the intensity peaked at 630 nm measured after 26.3 h (relative to the peak measured at 4.3 h), seems to indicate that the dimer- or oligomer-like aggregates, once formed, are hardly broken, and can even cause quenching if there is enough aggregation.

DCM's tendency to aggregate originates from the electric polarity of the molecules. One end of the molecule is donor-like dimethylamine. The other end is acceptor-like dicyanomethylene. When two DCM molecules are close enough, they will attract each other and tend to arrange themselves in an antiparallel manner. The attractive force between the two molecules in such a molecular pair or “dimer” should obviously be stronger than the weak van der Waals force existing between two individual molecules in an

organic solid. Therefore, DCM dimers, once formed, are more stable than individual DCM molecules. In contrast, as a nonpolar organic molecule, Alq shows hardly any tendency to aggregate.<sup>14</sup>

Most of the dye dopants currently used in OLEDs are strongly polar, so their aggregation is a general problem which leads to degradation of the OLEDs. Since it originates intrinsically from the materials themselves, the problem cannot be properly solved by changing the device configuration or varying operating parameters such as the driving current. Use of materials with steric hindrance or consisting spiro-linked compounds may suppress occurrence of the phenomenon to a certain extent,<sup>15,23</sup> but it is more favorable to choose nonpolar materials if possible.

In summary, DCM molecules doped in Alq have a tendency to aggregate and permeate, both at room temperature, and at much lower temperatures. As a result of aggregation and permeation, the OLEDs, using Alq:DCM as the red emitter, degrade seriously over a period of time. The problem is intrinsically related to the electric polarity of the material itself. Thus, nonpolar dyes should be more suitable as dopants for the OLEDs.

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