Doped organic electroluminescent devices with improved stability

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Remarkable improvement in stability has been demonstrated in an organic electroluminescent (EL) device using a doped emitter consisting of 8-hydroxyquinoline aluminum (Alq) as the host and N,N-dimethylquinacridone (DMQA) as the emissive dopant. A luminance half-life on the order of about 7500 h has been achieved in the DMQA/Alq EL device, operating under a constant current of 20 mA/cm^2 and starting at a high luminance of 1400 cd/m^2. The improved stability was attributed to the elimination of intermolecular hydrogen bonding between the dopant molecules. © *1997 American Institute of Physics.* [S0003-6951(97)01413-7]

Organic electroluminescent (EL) devices based on vapor-sublimed 8-hydroxyquinoline aluminum (Alq) thin films have been shown to be relatively stable. A luminance half-life[1] of about 4000 h has been obtained for a multilayer EL device with an undoped Alq emitter, operating at an initial brightness of about 500 cd/m^2. It is also known that the EL efficiency[2] can be significantly improved with the use of a doped emitter layer where a highly fluorescent dye is introduced as the more efficient emitting center in a host matrix such as Alq. Using such a scheme, EL devices with various dopant/host pairs have shown quantum efficiency as high as 4%–5% in photons per injected charge[3] and a corresponding luminance efficiency of 5–10 ℓ/w for the green[4] and 1–2 ℓ/w for the blue EL devices.[5] Specific dopant/host pairs have been found to provide enhanced operational stability as shown, for example, by Van Slyke *et al.*[6] for the perylene doped blue EL and by Sano *et al.*[7] for the rubrene doped green EL. However, EL instability could also rise due to the presence of undesirable dopants. Therefore, it is important to be able to correlate the EL stability with the chemical constitution of the dopant species. In this letter, we report a high-performance doped organic EL device with both enhanced efficiency and stability and show that the operational stability is critically dependent on the choice of dopant molecules.

Figure 1 shows the EL device configuration and the molecular structures of the organic materials used in the various layers. The sequence of the organic layers constructed on the (ITO) glass substrate was CuPc/NPB/doped Alq/undoped Alq. The ITO glass was obtained from Donnelly Applied Films or Balzer and the ITO layer was typically 300 Å thick with a sheet resistance of about 100 ohms/square. Prior to the organic layer deposition, the substrate glass was thoroughly cleaned by scrubbing, ultrasonication in a detergent, vapor decreasing, and irradiation in a UV-ozone chamber.

All organic layers wee prepared in a vacuum coater (10E-6 Torr base pressure) by vapor deposition. The resistably heated elements for the evaporate source materials were tantalum boats and the substrates were nominally unheated during deposition. The source to substrate distance was about 30 cm. The deposition rate for the organic layers was typically 4–5 Å/s. For the doped emitter layer, the deposition rates for the host material and the dopant were independently controlled by two quartz crystal oscillators, allowing the composition, i.e., the dopant concentration in Alq, to be adjusted. Following the deposition of all organic layers, a Mg:Ag (10:1 in volume ratio) layer forming the top cathode was deposited by coevaporation with a deposition rate of 10 Å/s for Mg in the same vacuum chamber without vacuum break. Finally, the EL device was encapsulated in a dry argon glove box for protection against the ambient environment.

The luminance output and chromaticity values were measured using a Photo Research PR650 spectrophotometer. A dc voltage or current source was used to trace the current–voltage characteristics. For operational stability testing, a constant current source was modified to include a reverse voltage component in its temporal wave form. This excitation was equivalent to an asymmetric ac power source providing a constant current excitation to the EL device in one half-cycle and a constant voltage bias (~14 V) in the other half-cycle at 1 kHz frequency. The light output and the forward bias voltage of the EL device under test were monitored continuously.

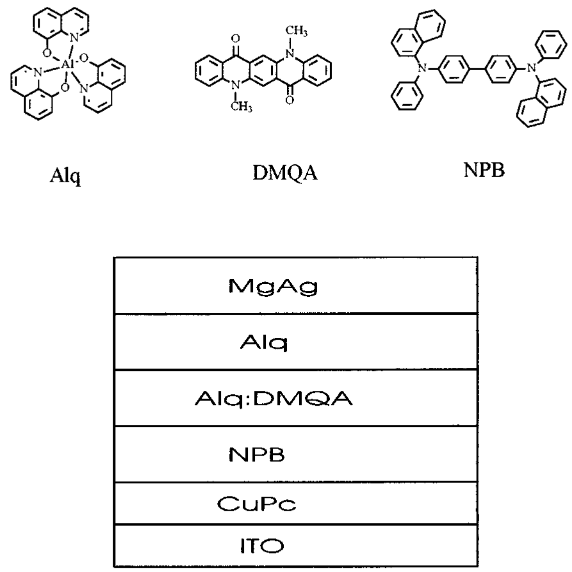

FIG. 1. Organic EL configuration and molecular structures.

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TABLE I. Luminance data of DMQA/Alq EL devices.

DMQA % in Alq	0.00	0.26	0.40	0.80	1.40	2.50
Lum. output (cd/m^2)	518	1147	1322	1462	1287	1027
Efficiency (cd/A)	2.59	5.74	6.61	7.31	6.44	5.14
CIE_x	0.3872	0.3876	0.3785	0.3922	0.4046	0.4095
CIE_y	0.5469	0.5858	0.5995	0.5901	0.5799	0.5742
EL peak (nm)	544	540	540	544	544	544
$T_{1/2}$ (h)	4200	7335	7500	7340	5450	3650

The luminance data of a series of Alq:DMQA EL devices are summarized in Table I. These EL devices have a common structure as follows: ITO/CuPc (150 Å)/NPB (600 Å)/Alq:DMQA (375 Å)/Alq (375 Å)/MgAg (2000 Å), where the DMQA concentration in the Alq:DMQA emitting layer is between 0% (undoped) and 2.5% (by mole). The luminance outputs, efficiencies, color coordinates, and peak wavelengths were measured at 20 mA/cm^2. It can be seen that the EL efficiency of the doped devices is significantly higher than that of the undoped Alq device, indicating that the excitation energy transfer from the Alq host to the N, N-dimethylquinacridone (DMQA) dopant is highly efficient. The optimum DMQA concentration in Alq is about 0.8%, providing an EL efficiency of 7.3 cd/A and an output of 1462 cd/m^2. With increasing DMQA concentrations, the EL efficiency decrease steadily and the EL spectra are slightly redshifted and broadened. These observations can be generally attributed to the formation of dimers and higher oligmers of DMQA molecules in the Alq host.

Figure 2 shows the relative luminance decay curves for the same series of EL devices. The excitation condition was as follows: 40 mA/cm^2 constant current in forward bias and ~14 V constant voltage in reverse bias. The waveform duty cycle and frequency were 50% and 1 kHz respectively, providing for an average excitation current of 20 mA/cm^2. The ac excitation waveform has been shown to be useful in minimizing the voltage rise during the stability run. For comparison between EL devices, the initial luminance outputs have been normalized to unity and their absolute luminance values are indicated in Table I. The stability run was continuously monitored for well over 9000 h for this series of EL devices. It can be seen that the relative luminance decay rate of the EL devices, regardless of the dopant concentration, is faster during the initial stage of the stability run and becomes progressively slower with continuous operation. The initial decay rate (first 1000 h) ranges from 7.7% to 21% per 1000 h with a considerable scatter among the data, but the long-term decay rate (beyond 5000 h) becomes almost constant and independent of the dopant concentration with an average value of about 3.2% per 1000 h. Figure 3 shows the corresponding forward bias voltage Vs operational time. The overall voltage rise for this series of cells is about 2 V in this period and, similar to the luminance decay, the voltage rise is considerably faster at the initial times. The EL spectra remain relatively unchanged over the course of the stability run, indicating that the relative contribution of various emitting species is unaffected.

A common measure of the operational stability is half-life, $T_{1/2}$, which is defined as the time to half-luminance with the EL device operating under constant current. The $T_{1/2}$ values for the DMQA/Alq doped devices, extracted from Fig. 1, are listed in Table I. It can be seen that $T_{1/2}$ appears to vary considerably among the EL devices, from about 7500 h for the 0.8% doped emitter to 3650 h for the 2.5%. However, this variation in $T_{1/2}$ is largely due to the difference in the decay rates observed in the beginning of the stability run. As shown in Fig. 2, the actual variation in stability among this

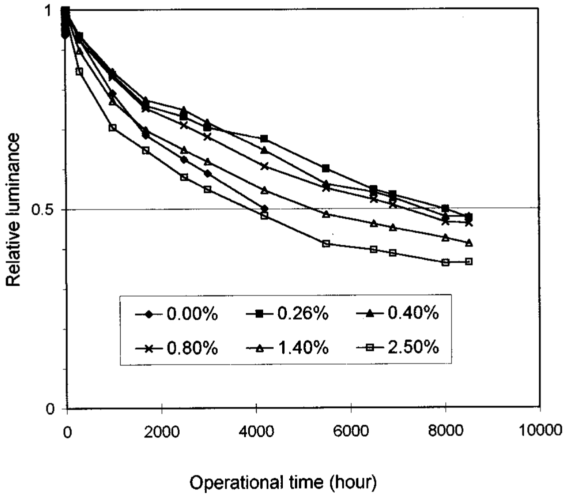

FIG. 2. Relative luminance decay curve of DMQA/Alq devices driven by an average constant current of 20 mA/cm^2. The initial luminance values are listed in Table I.

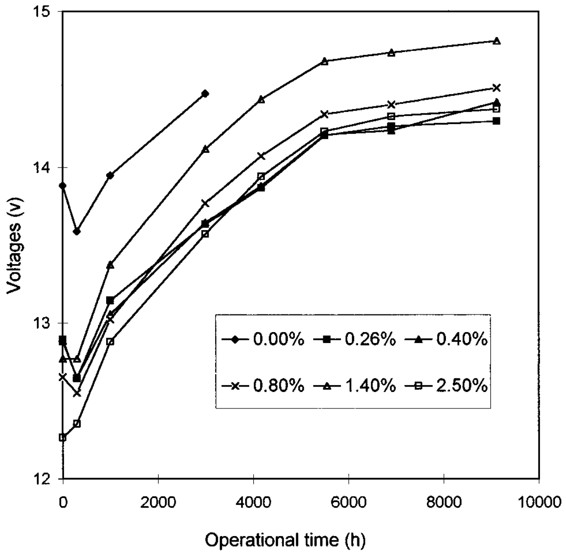

FIG. 3. Relative voltage rise curves for DMQA/Alq devices driven by an average current of 20 mA/cm^2.

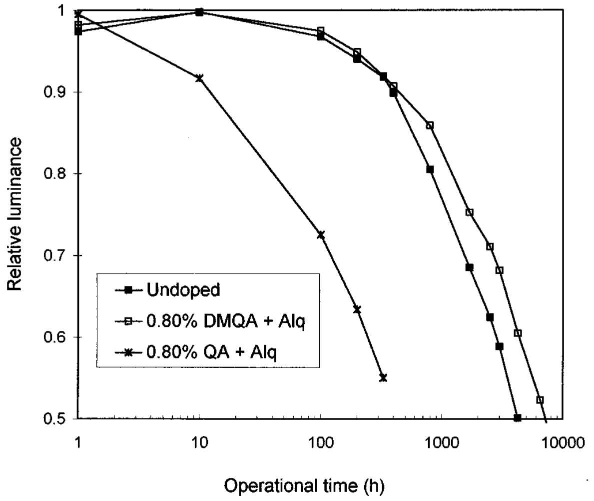

FIG. 4. Luminance decay curves of DMQA (0.80%)/Alq, QA (0.80%)/Alq, and undoped Alq devices.

series of doped devices is much less, considering that the luminance output from all devices after 9000 h are within 40% to 50% of their initial values. Thus, the effect of DMQA dopant on stability is largely reflected in the improvement in the luminous efficiency. Although the gain in relative stability is only marginal, the higher luminance output available from the more efficient DMQA/Alq emitter means that a longer operational lifetime is possible in most applications.

In this study, the design of a DMQA molecule was prompted by the fact that EL devices with the parent quinacridone molecule (QA) as the dopant was surprisingly unstable relative to the undoped device. This device instability is presumably related to the specific molecular structure of QA, notably its propensity for intermolecular hydrogen bonding. Figure 4 compares, in a logarithmic time scale, the luminance decay of EL devices with DMQA:Alq, QA:Alq, and undoped Alq as the emitters. Whereas the DMQA device has a half-life of about 7500 h, the QA device is rather short-lived with a half-life of about 500 h only. The initial luminance outputs from both EL devices are, however, quite comparable and the EL emission spectra are practically identical. Thus, the large difference in the operational stability between these two doped emitters is particularly remarkable considering that the basic EL characteristics are essentially similar. Both molecules are planar and the major structural difference lies in the substitution at the nitrogen atoms. In the case of the unsubstituted QA, the N–H moiety permits intermolecular hydrogen bonding between neighboring QA molecules,[8] favored by the planar geometry of the molecule. In the methyl-substituted DMQA, such an interaction is completely blocked due to the N–CH_3 moiety. The inferior stability of the QA doped device would lead one to believe that the tendency for intermolecular hydrogen bonding between QA molecules is the driving force for the formation of nonradiative centers, which are responsible for the loss of EL efficiency in operation. These nonradiative centers may be dimeric QA or other degradation products from a QA precursor.

In conclusion, a highly stable organic EL device has been demonstrated using DMQA/Alq as the doped emitter. A luminance half-life on the order of about 7500 h has been achieved. The improved stability was attributed to the elimination of intermolecular hydrogen bonding between the dopant molecules.

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[1] S. A. Van Slyke, C. H. Chen, and C. W. Tang, Appl. Phys. Lett. **69**, 2160 (1996).
[2] C. W. Tang, S. A. Van Slyke, and C. H. Chen, J. Appl. Phys. **65**, 3610 (1989).
[3] T. Sano, M. Fujita, T. Fujii, Y. Nishio, Y. Hamada, and K. Shibata, Extended Abstracts, The 41st Spring Meeting of the Japanese Society of Physics and Related Societies, 28p-N-2, 1994.
[4] T. Wakimoto, S. Kawami, K. Nagayama, Y. Yonemoto, R. Murayama, J. Funaki, H. Sato, H. Nakada, and K. Imai, Technical Digest, International Symposium on Inorganic and Organic Electroluminescence, 1994, p. 77.
[5] M. Matsuura, H. Tokailin, M. Eida, C. Hosokawa, Y. Hironaka, and T. Kusumoto, Proceedings of the 15th International Display Research Conference, Hamamatsu, Japan, Paper No. S11-2, 16–18 October, 1995, p. 269.
[6] S. A. VanSlyke, P. S. Bryan, and C. W. Tang, in *Proceedings of the Electroluminescence Workshop* (Wissenschaft and Technic, Berlin, 1996) p. 195.
[7] T. Sano, in *Proceedings of the Electroluminescence Workshop* (Wissenschaft and Technic, Berlin, 1996) p. 196.
[8] J. Kalowskii, W. Stampor, P. Di Marco, and V. Fattori, Chem. Phys. **182**, 341 (1994).