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Electroluminescence Enhancement by the Alignment of Doped Ionic Emissive Dyes along an External Bias Field

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A near-infrared asymmetric ionic emissive dye, LDS 821, exhibited a marked increase in EL quantum efficiency (ϕ_{ex}) in a constant current mode operation when doped in poly(vinylcarbazole) (PVK). Detailed studies on this EL enhancement phenomenon, together with differential scanning calorimetry (DSC) measurements, indicated that it was ascribable to the enhanced injection of charge carriers into the PVK layer due to a strong internal field generated by the alignment of the doped dyes along the bias field.

Keywords Near-infrared electroluminescence; Ionic emissive dye; Electroluminescence enhancement; Dye alignment; Internal field; Poly(vinylcarbazole)

INTRODUCTION

The origin and nature of internal fields built up during operation are important issues in current organic light-emitting diodes (LED) research because of their vital effect on organic LED characteristics. In this study, I have examined this issue by utilizing possible strong interactions between an asymmetric emissive ionic dye having a large permanent dipole moment ($\Delta\mu$) and external bias and/or the aforementioned internal fields.



FIGURE 1 The structure of LD S821 (a) and the LEDs fabricated in this study.

EXPERIMENTAL

The emissive ionic dye used was LDS 821, and was co-doped (1 wt%) in PVK with an electron transporting material, PBD (30 wt%), in a single-layer LED configuration (Figure 1). The methods of the LED fabrication and their spectroscopic (PL and EL) measurements were reported previously [1]. DSC measurements were performed in the temperature range between RT and 503 K on a MAC Science DSC 3100S at scan rates of 10 K/min in a 100 ml/min flow of nitrogen as a purge gas.

RESULTS AND DISCUSSION

The LED exhibited a near-infrared EL peaking at around 780 nm originating solely from the doped ionic dye. The band diagram depicted with a help of ionization potential measurements indicated that the doped LDS 821 acted as an effective carrier trapping and radiative recombination center for the EL. PL measurements confirmed that the excitation energy transfer from PVK to LDS 821 plays a negligible role in the EL process.

The LED manifested its unique features in various ways. In a constant current operation, for instance, there was a simultaneous increase in the EL intensity (thus, ϕ_{ex}) and decrease in the bias voltage with operating time (Figure 2a) without any substantial spectral change (Figure 2b). ϕ_{ex} reached the 1 %photons/electron level as a result of a similar increase by a factor of >80 from the initial value for constant 0.1

mA/cm^2 operation [1]. An additional time-dependent increase occurred even after the LED was stored under no bias field and subsequently reoperated at the same constant current, whereas ϕ_{ex} decreased after a reverse bias field application. Surprisingly, ϕ_{ex} increased after the LED had been stored under no bias field for 2 days, and relaxed to its initial value after about 6 days.

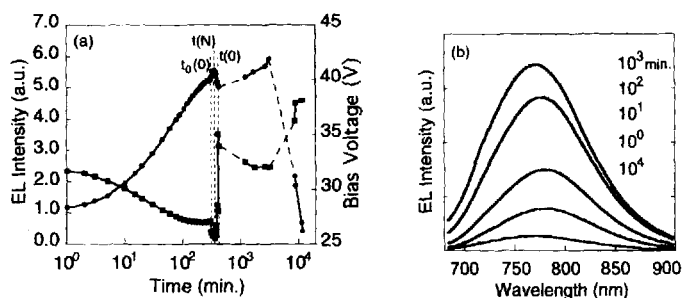


FIGURE 2 Operating time dependence of (a) EL intensity and bias voltage, and (b) EL spectrum. The symbol $t(N)$ in (a) means the sequential procedure of $t(-20)$ - $t(0)$ - $t(-30)$ - $t(0)$ - $t(-40)$. See ref. [1] for details.

Since the ϕ_{ex} increase accompanies a bias voltage decrease, an additional process, which is stable at room temperature and competes with the counter space charge internal field formed by trapped holes, must be the cause of the observed phenomena. The characteristics of the emissive dye (a rod-like structure, ionic nature and large intramolecular charge separation, together with the compositional similarity between this EL material and conventional PVK-based photorefractive materials [2], make it possible to ascribe the observed ϕ_{ex} increase to the doped dye alignment along the bias field. In practice, DSC measurements revealed that the glass transition temperature of this EL material is 125 °C, which is 70 °C lower than that of undoped PVK, and so the device temperature increase caused by continuous operation can facilitate dye alignment. This dye alignment model is schematically depicted in Figure 3. According as the dye alignment along the bias field proceeds, the developing polarization is canceled out in the bulk PVK

layer and is only effective at the interfaces of the PVK layer with the two electrodes. The strong internal fields at these interfaces thus induced, enhance the injection of both electrons and holes into the PVK layer and result in a ϕ_{ex} increase and a bias voltage decrease. The relaxation of the aligned LDS 821 is negligible at room temperature but is accelerated by a reverse bias field, which results in a ϕ_{ex} decrease and a bias voltage increase.

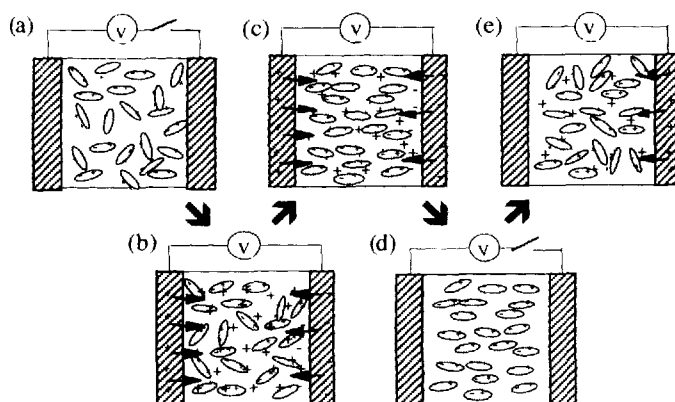


FIGURE 3 Schematic description of the dye alignment model, (a) before operation, (b) after short operation, (c) after long operation, (d) after bias field removal and (e) after reverse bias field application.

CONCLUSION

This study has demonstrated that ionic dyes are promising emissive materials for assessing the nature of the internal fields that build up in organic LEDs. In addition, if the observed phenomena are common to ionic dyes, their use can be a way to realize highly efficient organic LEDs.

References

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- [2] W. E. Moerner and S. M. Silence, *Chem. Rev.*, **94**, 127 (1994).