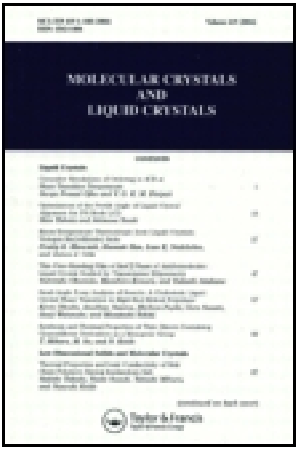

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Molecularly Doped Polymers for Organic Electroluminescent Devices

Junji Kido [a] , Masafumi Kohda [a] , Kenichi Hongawa [a] , Katsuro Okuyama [b] & Katsutoshi Nagai [a]

[a] Department of Materials Science and Engineering, Yamagata University, Yonezawa Yamagata, JAPAN

[b] Department of Electrical and Information Engineering, Yamagata University, Yonezawa, Yamagata, 992, JAPAN

Version of record first published: 24 Sep 2006.

To cite this article: Junji Kido , Masafumi Kohda , Kenichi Hongawa , Katsuro Okuyama & Katsutoshi Nagai (1993): Molecularly Doped Polymers for Organic Electroluminescent Devices, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 227:1, 277-283

To link to this article: http://dx.doi.org/10.1080/10587259308030981

Mol. Cryst. Liq. Cryst. 1993, Vol. 227, pp. 277–283
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

MOLECULARLY DOPED POLYMERS FOR ORGANIC ELECTROLUMINESCENT DEVICES

JUNJI KIDO*, MASAFUMI KOHDA*, KENICHI HONGAWA*,
KATSURO OKUYAMA† AND KATSUTOSHI NAGAI*
*Department of Materials Science and Engineering, †Department of Electrical and Information Engineering, Yamagata University, Yonezawa, Yamagata 992 JAPAN

Abstract Electroluminescent devices were fabricated using poly(methyl methacrylate) (PMMA) molecularly doped with triphenyldiamine derivative and tris(8–quinolinolato)aluminum(III) complex (Alq). A cell structure of glass substrate/indium–tin–oxide/doped PMMA/Mg:Ag was employed. Green emission with luminance of 920 cd/m^2 was achieved at a drive voltage of 17 V. The EL color was tuned to blue-green and yellow-orange by further doping the PMMA layer with suitable organic dyes.

INTRODUCTION

Electroluminescent (EL) devices based on organic thin layers have been studied extensively because of their possible application as large–area light–emitting displays.[1–18] Luminescence in such devices is generated by recombination of holes and electrons in the emitting layer, which excites the emitter material. Tang and VanSlyke[1] employed a double layer structure device to lower the drive voltage to a value of a few volts. Their device was fabricated by vacuum deposition, and consisted of a hole transport layer and a luminescent electron transport layer. In this case, recombination of injected electrons and holes takes place near the interface of the two organic layers, thus maximizing the recombination efficiency.

However, EL devices with vacuum deposited multilayers have problems such as recrystallization of the organic materials and the structural stability for the long term use. Therefore, employment of less crystalline polymeric materials may improve the lifetime of the devices, and single-layer-type device rather than multilayer-type device may achieve an improvement of structural stability. Recently, double-layer-type EL devices with a polymeric hole transport layer[7-10] and single-layer-type EL devices with intrinsically conductive polymers have been reported.[13-18]

We demonstrated the utility of molecularly doped polymers (MDPs) as the hole transport layer in double-layer-type devices[8] as well as the luminescent layer in single-layer-type devices.[11] MDPs are binary solid solution of a charge transporting molecules molecularly dispersed in an inert, inactive polymeric binders, and have been used as photoconductors in xerography.[19] Compared with intrinsically conductive polymers, MDPs are much more flexible in material design. For example, by selecting a proper dopant molecule and the concentration, it is possible to optimize carrier transport properties. In addition, the mechanical properties of the MDPs can be chosen by selecting the host polymer binder. Thus, this class of materials is ideally suited for the fabrication of EL cells.

In this paper, we report the improvement of the EL efficiency and the production of various EL colors by further doping the MDP layer with small amount of organic dyes with desirable colors.

EXPERIMENTAL

The MDP used in this study is the molecular dispersion of *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) and tris(8-quinolinolato)aluminum -(III) (Alq) complex in poly(methyl methacrylate) (PMMA). TPD has a high hole drift mobility of 10^{-3} cm^2/Vs,[20] and its hole transport properties in polymer matrix was reported.[20] Alq is a luminescent metal complex possessing electron transport properties and has been used as a luminescent layer in EL cells.[1,2,7-10] PMMA is optically and electronically inert, and has good film forming properties with a high glass transition temperature of 105 °C.[21]

Figure 1 shows the cell configuration and the molecular structures of the materials used in this study.

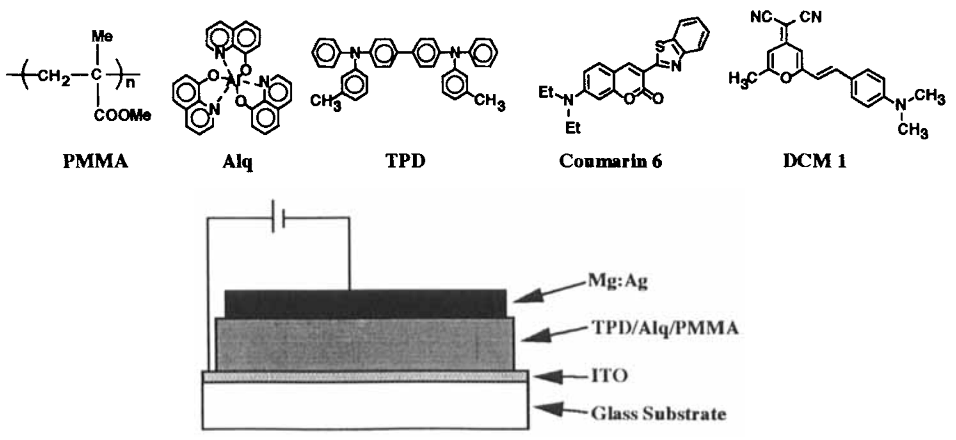

FIGURE 1 Configuration of EL cell and molecular structures of materials used.

The EL cell has a single-layer structure with doped PMMA sandwiched between electrodes. The doping concentration of TPD and Alq was kept constant at 50 wt% in total, and the molar ratio of TPD:Alq was 4:6. PMMA with a number average molecular weight of 100,000 was employed. A dichloromethane solution containing proper amounts of TPD, Alq, dye compounds and PMMA was dip-coated onto an ITO (indium-tin-oxide)-coated glass substrate with a sheet resistance of 10 Ω/□ (Furuuchi Chemistry Co. Ltd.). The thickness of the doped PMMA layer was 800–1,000 Å. Then, 2000 Å of magnesium and silver (10:1) were codeposited on the PMMA layer surface as the top electrode at 3×10^{-5} Torr. The substrate was kept at room temperature during the deposition and the deposition rate for Mg:Ag was 11 Å/s. The emitting area was 0.5x0.5 cm^2. Luminance was measured with a Minolta luminance meter LS-100 at room temperature under nitrogen atmosphere.

RESULTS AND DISCUSSION

In the photoluminescence (PL) of PMMA film containing both Alq and TPD, luminescence from Alq is observed even by the excitation of TPD.[11] This indicates that the excited energy is efficiently transfered from TPD to Alq. In the systems containing dopants such as coumarin 6 or DCM 1, luminescence from the dopants are observed. In these cases, the luminescence intensity is strongly dependent on the concentration of the dopants as shown in Fig. 2.

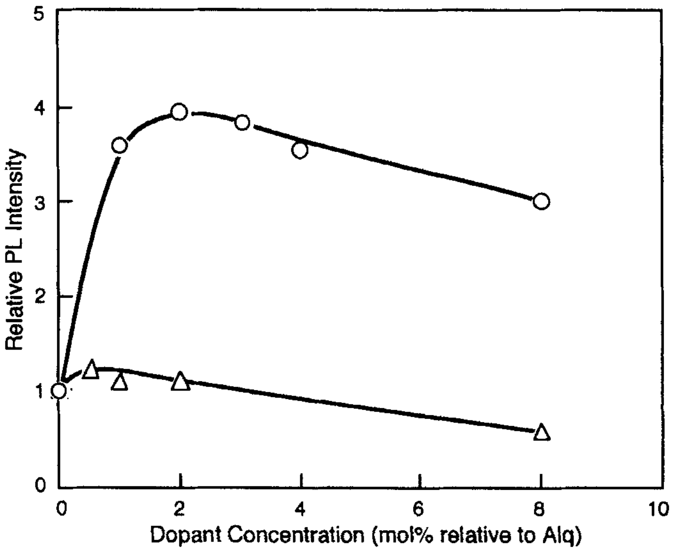

FIGURE 2 PL intensity of doped TPD/Alq/PMMA film as a function of dopant concentration. $\lambda_{EX} = 397$ nm.

The luminescence intensity shows maxima at 0.5~2 mol%, depending on the dopant, of the dopant concentration relative to Alq. A decrease in luminescence at higher concentration is observed, and is attributed to the concentration quenching or self quenching of the dopant themselves because these dye molecules are only weakly luminescent in the bulk state.

Figure 3 shows a typical current–voltage and luminance–voltage curves for an EL cell with TPD/Alq/PMMA system. Luminescence is observed from the EL cell when operated in a continuous dc mode for a forward bias with ITO at positive polarity, and it is proportional to the injection current as well as the bias voltage. Luminescence starts at a voltage as low as 6 V and the maximum luminance of 920 cd/m^2 and a current density of 170 mA/cm^2 are reached at 17 V. This is clearly visible in a lighted room: The luminance is much higher than that of a common CRT, which is less than 100 cd/m^2.

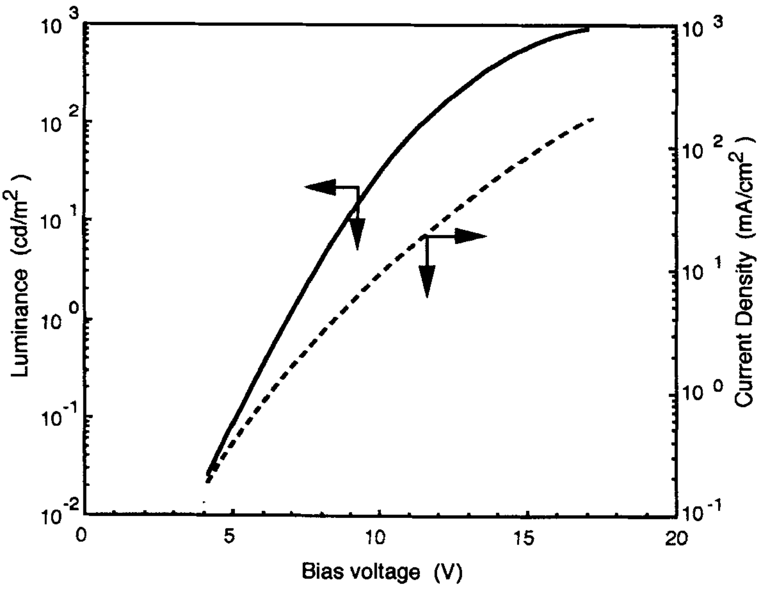

FIGURE 3 Luminance–voltage (solid line) and current–voltage (broken line) characteristics of a typical ITO/PMMA:TPD:Alq/Mg:Ag cell.

Electroluminescence from TPD/Alq/PMMA system is yellow-green. As we already reported,[11] the EL spectrum is identical to the PL spectrum of Alq, indicating that the electroluminescence originates from Alq. Although TPD is also a possible emitter, no electroluminescence from TPD is observed. This is probably due to higher excited energy level of TPD compared with that of Alq.

The EL color can be changed by further doping the PMMA layer with organic dye dopants. Fig. 4 shows the EL spectra of coumarin 6 or DCM 1 doped EL cells together with that of undoped cell. As observed in the PL of the doped systems, in case of coumarin 6, the EL spectrum is shifted to the shorter wavelength peaking at 500 nm which originates from the dopant. Similarly, in case of DCM 1, the EL spectrum is shifted to the longer wavelength peaking at 554 nm. The EL color is, thus, tuned from yellow-green to blue-green and yellow-orange, respectively. Similar results were obtained by Tang et al.[2] They doped the luminescent Alq layer in a double layer type device with those dopants, and observed EL from the dopants with higher efficiencies.

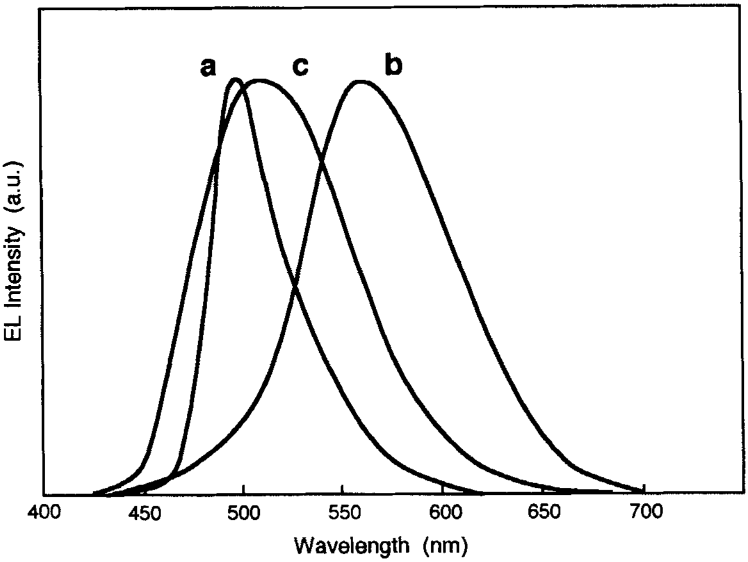

FIGURE 4 Normalized EL spectra of TPD/Alq/PMMA film doped with coumarin 6 (a) or DCM 1 (b), and undoped system (c). Dopant concentration=1mol% to Alq.

Carrier transport mechanism in MDPs is believed to be due to hopping between the dopant molecules of the same kind, which can be assumed to be an oxidation–reduction process. Thus, electrons and holes are transported in the polymer layer through Alq and TPD. Therefore, recombination of electrons and holes is, in fact, the reaction between $Alq^{-\bullet}$ and $TPD^{+\bullet}$. Alq is excited by the reaction and the excited energy is further transfered to the dopant, resulting in the luminescence from the dopants.

As shown in Fig. 5, luminance depends on the concentration of the dopant concentration. Luminance has maxima at 0.5–2 mol%, and decreases drastically with increasing the concentration. The tendency is similar to the results obtained for the photoluminescence of the doped PMMA film, but the enhancement factor is smaller than that for the PL. The PL intensity is increased by a factor of 4 for coumarin 6 system and by a factor of 1.3 for the DCM 1 system. On the other hand, luminance is increased by a factor of 1.3 for the coumarin system, and almost no increase in EL intensity is observed for the DCM 1 system. A clear explanation for the lower enhancement in EL efficiency is not available at present. Similar results were also observed by Tang et al. for the double layer type device.[2] They suggested that formation of charge transfer complex or exciplex between the dopants and diamine molecule near the interface of the two organic layers. However, our photoluminescence study shows no such complexes are formed between the dopants and TPD.

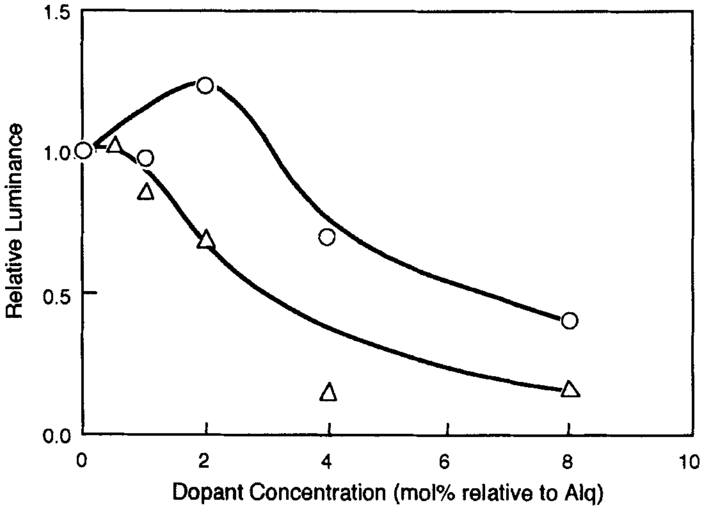

FIGURE 5 Relative luminance as a function of dopant concentration relative to Alq in TPD/Alq/PMMA. Current density = 100 mA/cm^2

In conclusion, the use of MDPs enables easy fabrication of EL devices in which carriers are injected through the dopants to the polymer layer resulting in electroluminescence. It was also demonstrated that various EL colors were obtained by further doping the polymer layer with the dopants possessing desirable colors.

REFERENCES

1. C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett., 51, 913 (1987).
2. C. W. Tang, S. A. VanSlyke, and C. H. Chen, J. Appl. Phys., 65, 3610 (1989).
3. C. Adachi, T. Tsutsui, and S. Saito, Appl. Phys. Lett., 56, 799 (1990).
4. C. Adachi, T. Tsutsui, and S. Saito, Appl. Phys. Lett., 57, 531 (1990).
5. J. Kido, K. Nagai, and Y. Ohashi, Chem. Lett., 657 (1990).
6. J. Kido, K. Nagai, Y. Okamoto, and T. Skotheim, Chem. Lett., 1267 (1991).

7. J. Kido, K. Nagai, Y. Okamoto, and T. Skotheim, Appl. Phys. Lett., 59, 2760 (1991).
8. J. Kido, K. Hongawa, M. Kohda, K. Nagai and K. Okuyama, Jpn. J. Appl. Phys., 31, L960 (1992).
9. J. Kido, Y. Guo, J. McBreen, K. Nagai and Y. Okamoto, Polym. Adv. Technol., in press.
10. T. Fujii, M. Fujita, Y. Hamada, K. Shibata, Y. Tsujino, and K. Kuroki, J. Photopolym. Sci. Technol., 4, 135 (1991).
11. J. Kido, M. Kohda, K. Okuyama and K. Nagai, Appl. Phys. Lett., 61, 761 (1992).
12. J. Kido, K. Nagai and Y. Okamoto, J. Alloys and Compounds, in press.
13. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, Nature, 347, 539 (1990).
14. P. L. Burns, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend, and R. W. Gymer, Nature, 356, 47 (1992).
15. D. Braun and A. J. Heeger, Appl. Phys. Lett., 58, 1982 (1991).
16. G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, Nature, 357, 447 (1992).
17. Y. Ohmori, M. Uchida, K. Muro, and K. Yoshino, Jpn. J. Appl. Phys., 30, L1938 (1991).
18. Y. Ohmori, M. Uchida, K. Muro, and K. Yoshino, Jpn. J. Appl. Phys., 30, L1941 (1991).
19. J. Mort and G. Pfister, in Electronic Properties of Polymers, edited by J. Mort and G. Pfister editors (Wiley, New York, 1982), Chap. 6, pp.215-265.
20. M. Stolka, J. F. Yanus, and D. M. Pai, J. Phys. Chem., 88, 4707 (1984).
21. Polymer Handbook 3rd Edition, edited by J. Brandrup and E. H. Immergut (Wiley, New York, 1989).