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

Charge Injection, Transport, Recombination and Generation of Neutral Excitations in Multilayer-Dye Electroluminescent Diodes

Tetsuo Tsutsui [a] , Ching Piao Lin [a] & Shogo Saito [a]
[a] Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, 816, Japan
Version of record first published: 04 Oct 2006.

To cite this article: Tetsuo Tsutsui , Ching Piao Lin & Shogo Saito (1994): Charge Injection, Transport, Recombination and Generation of Neutral Excitations in Multilayer-Dye Electroluminescent Diodes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 63-70

To link to this article: http://dx.doi.org/10.1080/10587259408039232

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 63–70
Reprints available directly from the publisher
Photocopying permitted by license only

CHARGE INJECTION, TRANSPORT, RECOMBINATION AND GENERATION OF NEUTRAL EXCITATIONS IN MULTILAYER-DYE ELECTROLUMINESCENT DIODES

TETSUO TSUTSUI, CHING PIAO LIN AND SHOGO SAITO
Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816, Japan

Abstract Emission characteristics of multilayer-dye electroluminescent diodes were discussed in terms of molecular structures of component dyes as well as multilayer device structures. Using the same dyes for dispersed dyes in polymer matrices, single-layer polymer-dispersed dye electroluminescent diodes were fabricated. The emission characteristics of polymer-dispersed dye diodes were discussed in relation with those of multilayer-dye diodes.

INTRODUCTION

In these several years, thin-film electroluminescent diodes (ELD) made of varieties of organic materials, such as sublimed dye films, fully conjugated polymer films, polymers with chromophores on skeleton-chains or side-chains and polymer-dispersed dye films, have been reported. It has been well recognized that basic working mechanism among those EL diodes is the same, even though molecular and aggregated structures of constituent materials are markedly different.

We have investigated the meaning of multilayer structures in ELD's which were composed of sublimed dye films and have found that the basic working principle of multilayer-dye ELD's is quite similar with that of fully conjugated polymer ELD's.[1,2] Because the designs of both device structures and constituent dye molecules in multilayer-dye ELD's have very high flexibility, studies on multilayer-dye ELD's are expected to provide important indications for the understanding of electronic nature of conjugated polymers. Very recently, it has been shown that polymer-dispersed dye ELD's also showed very similar electroluminescent characteristics with conventional multilayer-dye ELD's.[3,4] They have one of the simplest device structures; a polymer thin film in which a few kinds of dyes are molecularly dispersed is sandwiched between a pair of electrodes, and they are useful for clear-cut understanding of the working mechanism in

organic ELD's.

In this report, firstly we will briefly summarize our published results on multilayer-dye ELD's, and then explain our basic understanding for the working mechanism of multilayer-dye ELD's. Then we will show our recent data on polymer-dispersed dye ELD's. Dye molecules used in the multilayer-dye ELD's and the polymer-dispersed dye ELD's are almost the same, and thus direct comparisons of the emission behaviors between two types of ELD's are possible. In other words, one can discuss similarity and dissimilarity in charge injection, charge transport and recombination in multilayer-dye systems and polymer-dispersed dye systems.

One of the most important conclusions from these discussion is that the most essential electronic nature for electroluminescence is related to electronic structures of dye molecules themselves not to aggregated structures of molecules. This finding, we believe, is helpful for understanding the basic mechanism of electroluminescence in conjugated polymers.

MULTILAYER-DYE ELECTROLUMINESCENT DIODE

ELD's with two-layer structures are composed of transparent indium-tin-oxide (ITO) anode, a hole transport layer (HTL), an electron transport layer (ETL) and metal cathode (MgAg alloy film, for example). The HTL carries the roles of assisting the injection of holes from ITO and transport of the injected holes to the boundary of two organic layers, and the ETL has the function of assisting the injection of electrons from a metal cathode and the transport of the injected electrons. Recombination of holes and electrons occurs at the boundary regions between two organic layers. When the recombination region locates within an ETL, an ETL behaves as an emissive layer (EML).[5] On the other hand, we sometimes find the cases that a HTL behaves as an EML.[6] Thus the two layer devices are classified into two types; ITO/HTL/ETL(EML)/MgAg and ITO/HTL(EML)/ETL/MgAg. When bipolar materials which have the ability to carry both electrons and holes are available, one can use a three layer structure in which an independent thin EML is sandwiched between HTL and ETL; ITO/HTL/EML/ETL/MgAg.[7] Figure 1 demonstrates three typical device structures.[8]

We reported that TPD and PBD, the molecular structure of which are shown in Fig. 2, can be used as typical HTL and ETL materials, respectively. Here we show the electroluminescent behaviors of the ELD's which are composed of some EML materials with either HTL or ETL characteristics and those typical

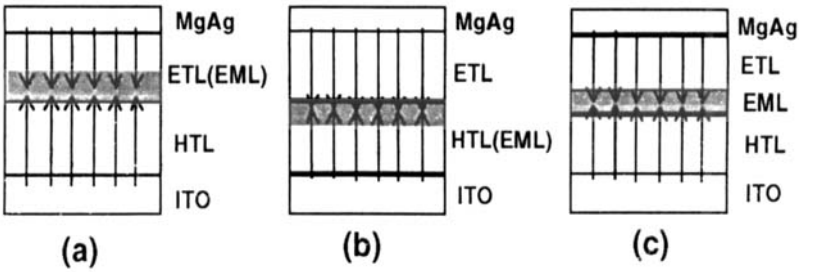
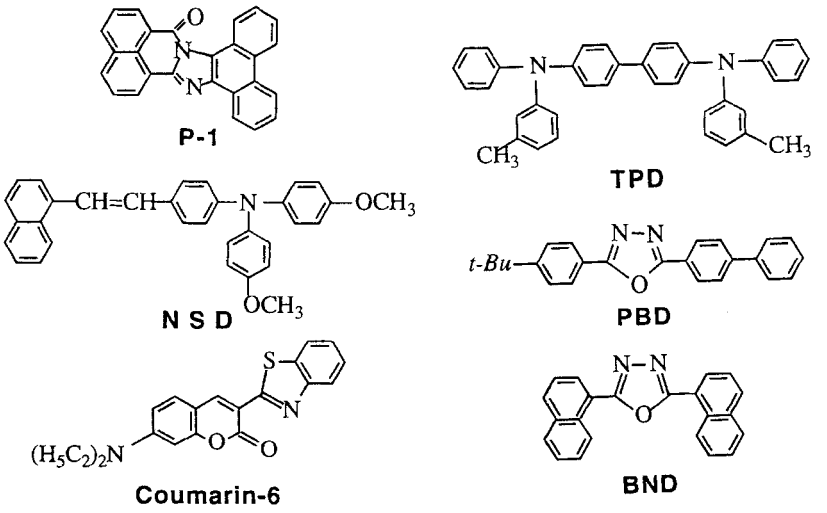


FIGURE 1 Three typical multilayer device structures. Charge recombination occurs within hatched regions.



F IGURE 2 Molecular structure of dyes used in this study.

charge transport material. Using a phthaloperinone derivative P-1 shown in Fig. 2, we fabricated two ELD's; a P-1 dye layer was combined with a TPD layer as a HTL (ITO/TPD/P-1/MgAg) and a P-1 layer was combined with a PBD as an ETL (ITO/P-1/PBD/MgAg). Both ELD's exhibited yellow emission due to the P-1 dye and we assured that the P-1 layer took a role of an EML in both devices. Figure 3 compares the luminance-current density relationships of two devices. The EL efficiency in the ITO/TPD/P-1/MgAg device is more than 4 orders of magnitude higher than that in the ITO/P-1/PBD/MgAg device.[9] The EL quantum efficiency is governed by three major factors, charge balance factor, γ, efficiency of production of singlet excited states, η_r and quantum efficiency of fluorescence ϕ_f.[1] Thus we

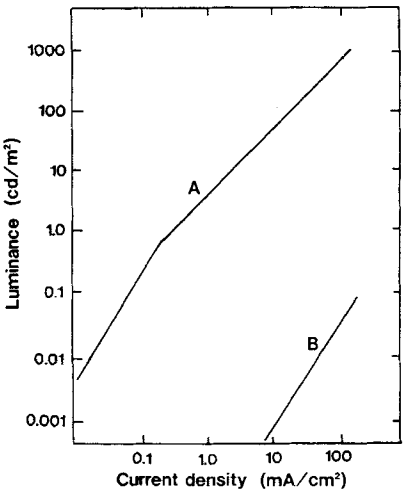


FIGURE 3 Luminance-current density relationships in ITO/TPD/P-1/MgAg (A) and ITO/P-1/PBD/MgAg (B) devices.

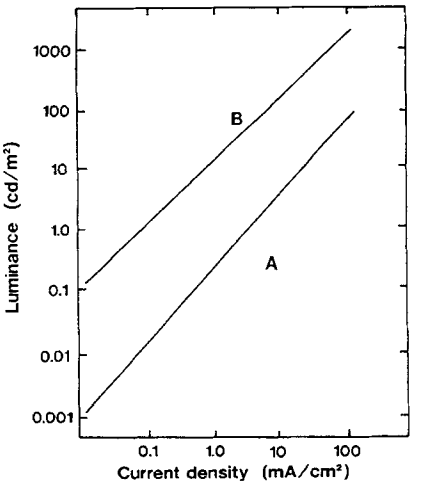


FIGURE 4 Luminance-current density relationships in ITO/TPD/NSD/MgAg (A) and ITO/NSD/PBD/MgAg (B) devices.

find that charge balance factor γ in two devices brings about large difference in EL efficiencies, because other two factors are not assumed to be sensitive to device structures. The large difference in EL quantum efficiencies can be understood if we assume that the P-1 dye has a typical electron transporting tendency.

Perfectly reversed situation is demonstrated using a NSD dye which is assumed to have a hole transporting tendency. Figure 4 compares luminance-current density relationships between two ELD's with the structures of ITO/TPD/NSD/MgAg and ITO/NSD/PBD/MgAg. The EL quantum efficiency is about two orders of magnitude higher, when the NSD layer is combined with a PBD layer as an ETL.

When good EML materials which behave as an EML are available, three-layer devices with an extremely thin EML can be fabricated. This is also one of the best examples that explain the roles of HTL, ETL and EML.[7,10]

These examples clearly demonstrate that appropriate combinations of two dye layers which behave as hole transport and electron transport layers are important for the attainment of high performance in multilayer-dye ELD's.

POLYMER-DISPERSED DYE ELECTROLUMINESCENT DIODE

Using the emissive dyes, P-1 and NSD demonstrated above, we fabricated polymer-dispersed dye ELD's. TPD as a HTL material and BND, which has a very similar molecular structure with PBD, as an ETL material were also employed. Polymer

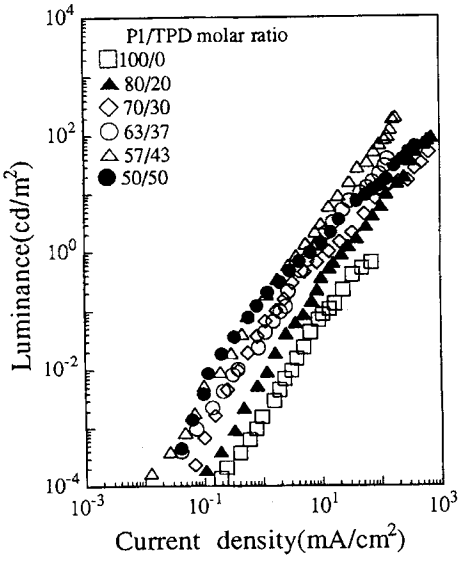


FIGURE 5 Luminance-current density relationships in single layer devices composed of 50 wt% P-1/TPD dyes and 50 wt% matrix polymer. P-1/TPD molar ratios are indicated in the figure.

dispersed-dye films were prepared with spin-coating from dichloromethane solutions of dyes and binder polymer on ITO substrates. The content of inert binder polymer was fixed to be 50 % by weight in all devices. A top cathodes were vacuum-deposited MgAg alloy films.

Figure 5 shows the luminance-current density relationships of the polymer-dispersed dye ELD's made of P-1 and TPD. The molar ratios of P-1 and TPD were changed keeping total weight content of dye components to be 50 wt%. The highest EL efficiency was observed when the P-1/TPD ratio was 57/43. The ELD containing only the P-1 component showed about two orders of magnitude lower efficiency. This observation can be well corresponded to the case of multilayer-dye ELD's. The stacking of the TPD layer with hole transport capability and the P-1 layer with good electron transport capability was the origin of balanced injection and transport of holes and electrons in the multilayer-dye ELD's. On the other hand, incorporation of both hole transport and electron transport molecules into a polymer film is necessary for balanced injection and transport of holes and electrons. In other word, molecules dispersed in a polymer matrix surely carry the function of charge-injection and transport.

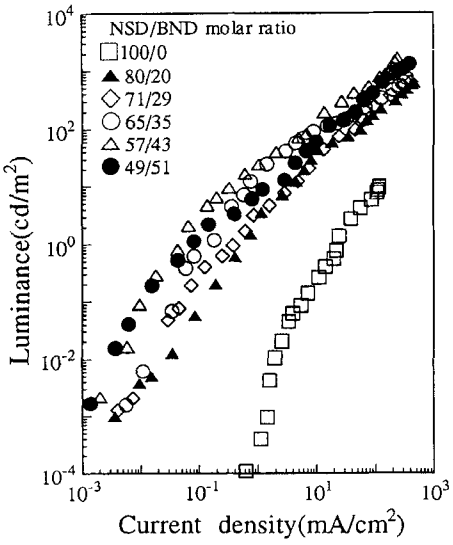


FIGURE 6 Luminance-current density relationships in single layer devices composed of 50 wt% NSD/PBD dyes and 50 wt% matrix polymer. NSD/BND molar ratios are indicated in the figure.

Figure 6 demonstrates the case of another combination of dyes in polymer dispersed dye ELD's. The combination of BND as an electron transport dye and NSD as a hole transport dye with emission capability was examined. The device with a single component of NSD showed more than two orders of magnitude lower efficiency than that with adequate compositions of two dyes. Emission was due to NSD molecules as a hole transport molecules. This observation gives clear contrast to Fig.5, because P-1 molecules as an electron transport molecules emit light in the P-1/TPD combination.

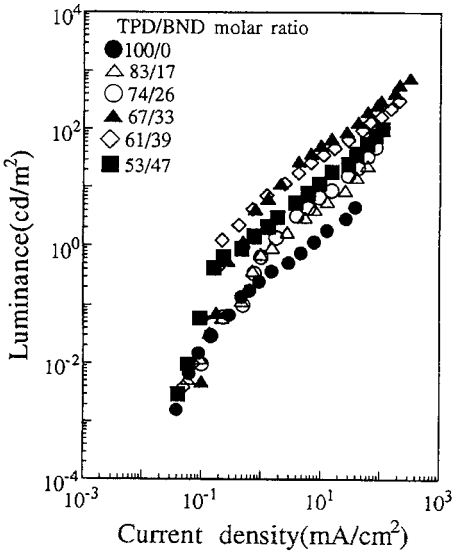


FIGURE 7 Luminance-current density relationships in single layer devices composed of 50 wt% TPD/BND dyes and 50 wt% matrix polymer. One wt% of coumarin-6 was added as emissive centers. TPD/BND molar ratios are indicated in the figure.

The third case of polymer-dispersed dye ELD's is a three-component system composed of hole transport molecules (TPD), electron transport molecules (BND) and small amount of emissive molecules (coumarin-6). When TPD and BND dyes were dispersed in a polymer matrix, weak emission which was assumed to originate from exciplex of TPD and BND was detected. Bright green emission due to counmarin-6 molecules was observed, when 1.0 wt% of coumarin-6 was added to the system. Figure 7 shows the luminance-current density relationships in the devices composed of TPD, BND and coumarin-6. The EL efficiencies

were dependent on TPD/BND ratios, while emission from cuomarin-6 molecules was observed in all compositions. Our observations on the ternary system of TPD, BND and coumarin-6 demonstrate that the singlet excited states of cuomarin-6 molecules are produced by either the recombinations of holes and electrons just on the coumarin-6 molecules or efficient energy transfer of excited states takes place from charge transport dye molecules, at which charge recombination occurs, to coumarin-6 molecules . Thus we can easily identify the roles of hole transport sites, electron transport sites and emissive centers.

CONCLUSIONS

It has been demonstrated that charge injection, transport and recombination processes in single-layer, multi-component polymer-dispersed dye ELD's are quite similar to those in multilayer-dye ELD's. In polymer-dispersed dye ELD's, dye molecules are assumed to be uniformly dispersed with an average distance of about 1.2 nm. Therefore electrons and holes must move via hopping among isolated molecules, and the recombination of electrons and holes takes place on isolated molecules. In the case of multilayer-dye ELD's, exactly the same processes should be assumed to occur, even though dye molecules are more densely packed in sublimed films. This is a quite simple but clear picture for charge-injection type electroluminescence common to every molecular system.

REFERENCES

1. T. Tsutsui and S. Saito, in Intrinsically Conducting Polymers: An Emerging Technology, edited by M. Aldissi (Kluwer Academic Pub., Netherlands, 1993), p.123.
2. T. Tsutsui, E. Aminaka, Y. Hamada, C. Adachi and S. Saito, **Proc. SPIE, 1910**, 180 (1993).
3. J. Kido, M. Kohda, K. Okuyama and K. Nagai, **Appl. Phys. Lett., 61**(7), 761 (1992).
4. J. Kido, M. Kohda, K. Nagai and K. Okuyama, **Proc. SPIE, 1910**, 31 (1993).
5. C. W. Tang and S. A. VanSlyke, **Appl. Phys. Lett., 51**, 913 (1987).
6. C. Adachi, T. Tsutsui and S. Saito, **Appl. Phys. Lett., 55**, 1489 (1989)
7. C. Adachi, T. Tsutsui and S. Saito, **Appl. Phys. Lett., 57**, 531 (1990).
8. C. Adachi, T. Tsutsui and S. Saito, **Optoelectronics-Devices and Technologies, 6**(1), 25 (1991).
9. T. Tsutsui, C. Adachi and S. Saito, **Synthetic Metals, 41-43**, 1193 (1991).
10. M. Era, C. Adachi, T. Tsutsui and S. Saito, **Chem. Phys. Lett., 178**(5,6), 488 (1991).