Extended molecular design concept of molecular materials for electroluminescence: sublimed –dye films, molecularly doped polymers and polymers with chromophores

T. Tsutsui, E. Aminaka, C. P. Lin and D. -U. Kim

Email alerting service	Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click **here**

Extended molecular design concept of molecular materials for electroluminescence: sublimed-dye films, molecularly doped polymers and polymers with chromophores

By T. Tsutsui, E. Aminaka, C. P. Lin and D.-U. Kim

Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816, Japan

Electroluminescent (EL) devices with multilayer structures which are composed of two or three vacuum-sublimed dye films have been shown to exhibit high device performances. The working mechanism for charge-injection-type EL devices is reviewed and then the design of dye molecules used for hole transport, electron transport and emissive layers for multilayer EL devices are summarized. It is also demonstrated that the molecular design concept of dye films is applicable for the cases of polymer-dispersed dye systems. The possibility of extension of the molecular design concept to polymers with chromophores in skeletons is discussed. In addition, the importance of the adoption of multilayer structures for obtaining high EL efficiency is discussed.

1. Introduction

In the past several years, much progress has been made in the research and development in electroluminescent (EL) devices made of molecular materials. It has been shown that a variety of molecular materials such as vacuum-sublimed dye films, fully π-conjugated polymers, polymers with chromophores on skeletal-chains or side-chains and polymer-dispersed dye films can be used for EL devices. It has been well recognized that the basic working mechanism among those EL devices is the same, even though not only molecular structures of constituent materials, but also device structures, are markedly different (Tsutsui & Saito 1993; Tsutsui *et al.* 1994*a*, *b*).

Among a variety of EL devices, multilayer-structure EL devices made of vacuum-sublimed dye films exhibit the highest performances. Because the designs of both device structures and constituent dye molecules in multilayer-dye EL devices have high flexibility, studies on multilayer-dye EL devices are expected to provide important indications for the establishment of material design concept for EL devices. Thus, we have investigated the meaning of multilayer structures in multilayer EL devices which were composed of sublimed dye films (Tsutsui *et al.* 1993). Through our systematic studies on multilayer EL devices made of vacuum-sublimed films, we have established our key understanding that the basic EL mechanism from charge injection to emission is common in all molecular materials, since emissions in EL devices are via neutral excitations. According to this basic understanding, we have proposed that the concept for materials design for dye-sublimed multilayer films can be extended to fully π-conjugated polymer films, polymer films with chromophores

on main-chains or side chains and even polymer-dispersed dye systems. For example, dyes used for multilayer sublimed-dye EL were utilized for charge transport and emissive dyes in polymer-dispersed dye EL, and the roles of dyes as charge transport, charge recombination and emission in multilayer dye films and polymer-dispersed dye systems were almost the same (Tsutsui *et al.* 1993). The situations have been very similar in the design of polymers with chromophores in skeletal or side chains. We have demonstrated some examples for systematic molecular design of polymers with charge transport and emissive chromophores in their skeletons (Kim *et al.* 1995*b*; Tsutsui & Kim 1996).

In this paper, we show our basic understanding for the working mechanism for charge-injection-type EL through the derivation of some basic formulae which quantitatively describe EL efficiencies. Then we will demonstrate some examples of our molecular design of molecular materials for electroluminescence.

2. Quantum efficiency and energy efficiency of electroluminescence

Apparently, EL devices made of molecular materials behave very similarly to conventional LED's made of inorganic semiconductors and thus they are called organic or polymer LED's. One should be very careful, however, that detailed behaviours of conventional LED's and EL diodes made of molecular materials are quite different. This difference is originated from two intrinsically different electronic and optical characteristics between conventional inorganic semiconductors and so-called molecular semiconductors. It should be emphasized here that the estimation of EL efficiencies are quite simple once we accept two basic assumptions concerning the working mechanism of charge-injection-type EL made of molecular materials.

First, all the molecular materials useful for EL are insulators. As early studies on EL in anthracene single crystals clearly indicate, anthracene is a typical insulator with resistivity of 10^{20} Ω cm (Pope & Swenberg 1982). Typical vacuum-sublime dye films are known to have resistivities of the order of 10^{15} Ω cm. Even one of typical π-conjugated polymers, PPV, has an intrinsic resistivity of 10^{16} Ω cm (Tokito *et al.* 1986). This assumption means that no charges are present in EL devices without charge injection and we only have to turn our attention to the behaviours of injected charges from electrodes. In other words, we deal with EL devices not under electrostatic equilibrium but under dynamic charge equilibrium when devices are under operation. All charges are assumed to behave as space-charges in EL devices and no local charge neutrality is expected within devices.

Second, neutral excited states, typically singlet excitations, are produced by charge recombination and emission is due to emissive transitions from neutral excited states to ground states. No experimental evidence on the direct emission due to the recombination of positive and negative charges in EL devices made of molecular materials has been provided.

Figure 1 represents the elementary processes beginning from recombination of holes and electrons and ending by taking out emitted light outside of an EL device. The external efficiency and the internal efficiency are connected by the factor η_{ext}, which is approximately evaluated by using refractive index of emissive medium n:

$$\eta_{\text{ext}} = 1/(2n^2). \tag{2.1}$$

When external quantum EL efficiency, $\eta_\phi(\text{ext})$ is defined to be the ratio of numbers of emitted photons outside a device divided by apparent number of charges injected
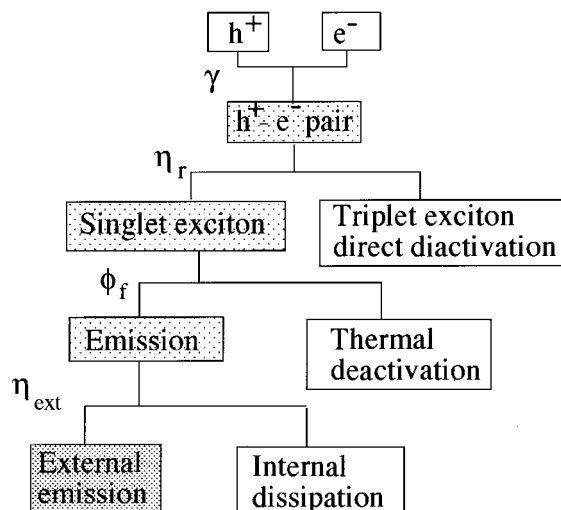
Figure 1. Schematic representation of the elementary processes for charge recombination, production of singlet excitons, emission and external emission.

into a device, and internal quantum efficiency, η_ϕ is defined to be the number of photons produced within a device divided by apparent number of charges injected, the $\eta_\phi(\mathrm{ext})$ is expressed as

$$\eta_\phi(\mathrm{ext}) = \eta_\phi \eta_{\mathrm{ext}}. \tag{2.2}$$

Using charge balance factor γ, efficiency of production of singlet excitons η_r and quantum efficiency of fluorescence ϕ_f, internal quantum EL efficiency, η_ϕ, is given by

$$\eta_\phi = \gamma \eta_r \phi_\mathrm{f}. \tag{2.3}$$

The definition of charge balance factor γ is not very clear and some detailed examination should be added. The γ is defined by equation (2.4), using the apparent number of charges injected into a device, which is obtained experimentally from circuit current J, and the number of electron–hole pairs, which is estimated from the current disappeared within a device J_r:

$$\gamma = J_\mathrm{r}/J. \tag{2.4}$$

A quite simple assumption, which represents the mass balance and charge neutrality of holes and electrons depicted in figure 2, may well explain the meaning of J_r. The amount of holes and electrons injected from an anode and a cathode are expressed by J_h and J_e. The amount of holes crossing through the organic layer–cathode interface, and that of electrons crossing through the organic layer–anode interface, are given by J_h' and J_e'. It is now possible to derive

$$J = J_\mathrm{h} + J_\mathrm{e}' = J_\mathrm{e} + J_\mathrm{h}' \tag{2.5}$$

and

$$J_\mathrm{r} = J_\mathrm{h} - J_\mathrm{h}' = J_\mathrm{e} - J_\mathrm{e}'. \tag{2.6}$$

Although there exist no direct means to evaluate the value J_r, one can discuss J_r values based on the examinations on charge recombination regions. When a narrow charge recombination region is located within an emissive layer, all holes and electrons are assumed to be consumed for recombination and $J = J_\mathrm{r}$. Thus, $\gamma = 1.0$
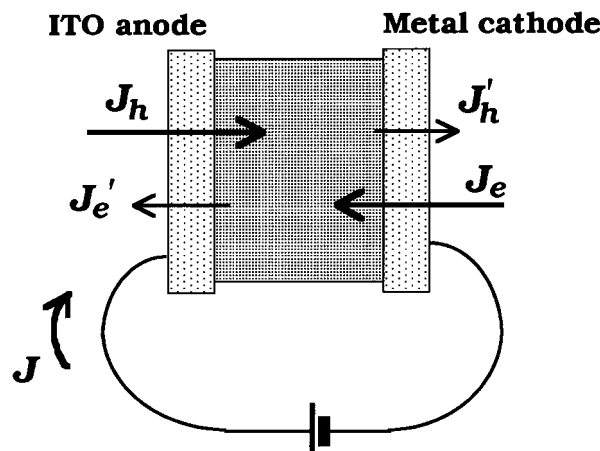
Figure 2. Positive and negative charges injected and passed through an EL device.

(Aminaka *et al.* 1996). On the other hand, if major parts of electrons go through out of a device and all the holes injected are used for recombinations ($J_{h}' = 0$, $J_{e}' > 0$), $J_e \gg J_h$ and $J_r = J_h \ll J_e = J$. Thus, γ is assumed to be much less than unity.

The relationship between the energy efficiency (internal) η_E, which is defined by the ratio of emitted light power inside a device and the electric power applied (JV), and the quantum efficiency (internal), is given by

$$\eta_E = \eta_\phi(\varepsilon_p/eV), \tag{2.7}$$

where ε_p and V denote the photon energy of emitted light and applied voltage, respectively. It should be emphasized that equation (2.7) is not an approximate relation, but the exact relation that connects energy efficiency and quantum efficiency. Equation (2.7) is easily derived from the definitions of quantum efficiency and energy efficiency.

One should note that applied voltage is only included in the expression of energy efficiency and that quantum efficiency is not directly related with applied voltage. In other words, so-called barriers for charge injection have no explicit concern with quantum efficiency. The balance of injected holes and electrons govern quantum efficiency and the applied voltage needed for injection and holes determine energy efficiency. These are the most important key issues for understanding EL efficiencies in charge-injection-type EL devices.

Thus, the keys for attaining ultimate high EL efficiencies are summarized in the following four issues:

(1) The attainment of unity charge balance factor γ is the most important. $\gamma = 1.0$ is expected to be attained by the use of multilayer structures, as is described in the next section.

(2) The maximum value for the efficiency of production of singlet exciton η_r is assumed to be $\frac{1}{4}$, due to spin statistics for production of singlet and triplet states by charge recombination (Helfrich & Schneider 1966). This factor is assumed to be insensitive to both device structures and molecular materials used.

(3) The quantum efficiency of fluorescence ϕ_f is mainly governed by the intrinsic electronic nature of molecular materials used and one should be careful in selecting appropriate emissive centres. Possible quenching processes of singlet excitons may cause a decrease of quantum efficiency of fluorescence in some cases.
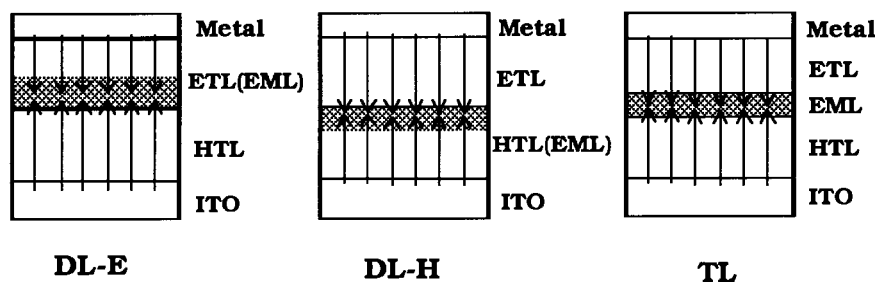
Figure 3. Three typical multilayer device structures. DL-E and DL-H are double-layer devices and TL is a triple layer device. Charge recombination and emission are assumed to occur within hatched regions.

(4) The factor determining energy efficiency is ε_p/eV. This factor is assumed to be less than unity since some extra energy is consumed before the production of thermally relaxed singlet excitons. Voltage losses due to charge injection barriers and charge transport resistance, and excess energy consumed for thermal relaxations of produced singlet excitons, are the main origins of causing the decrease in the ε_p/eV factor to less than unity.

3. Design of device structures and dye molecules for vacuum-sublimed dye multilayer devices

EL devices with double-layer structures are composed of a transparent indium-tin-oxide (ITO) anode, a hole transport layer (HTL), an electron transport layer (ETL) and metal a cathode (MgAg alloy film, for example). The HTL carries the roles of assisting the injection of holes from ITO and transporting 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 transporting 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, the ETL behaves as an emissive layer (EML). On the other hand, we sometimes find to be the case that a HTL behaves as an EML. Thus, the double-layer devices are classified into two types: DL-E type (ITO/HTL/ETL(EML)/MgAg) and DL-H type (ITO/HTL(EML)/ETL/MgAg). When bipolar materials, which have the ability to carry both electrons and holes, are available, one can use a triple-layer structure in which an independent thin EML is sandwiched between HTL and ETL; TL type (ITO/HTL/EML/ETL/MgAg) (Adachi *et al.* 1990*b*). Figure 3 demonstrates three typical device structures.

An aromatic diamine, N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD), has been used as a typical HTL material, which shows excellent hole injection and transport capability with good electron blocking capability at a HTL/ETL boundary. Although TPD has superior characteristics for HTL, the stability of vacuum-sublimed thin TPD films is not so high, due to its low glass transition temperature. Several other HTL materials have been tested, but no molecular material with better performance than TPD has been found so far. Insertion of another hole transport layer between the ITO electrode and the TPD layer was shown to be effective for getting improved performance (Shirota *et al.* 1993). Starburst polyamine (m-MTDATA) has been shown to be adequate for this purpose.

806   *T. Tsutsui, E. Aminaka, C. P. Lin and D.-U. Kim*

A lot of ETL materials which behave as an EML have been reported. For example, Alq is known to be one of the best ETL (EML) materials and many other ETL (EML) materials are also available. However, if we want to use the DL-H structure or the triple-layer structure with an independent EML, particular ETL materials with high exciton energies are required. Major requirements for this type of ETL materials are summarized as follows.

(1) Materials give stable and uniform vacuum-sublimed thin films.

(2) Materials have large electron affinity for electron injection.

(3) Materials have high electron mobility for transport of electrons.

(4) Materials have large ionization potential for preventing the arrival of holes to a metal cathode without recombination with electrons.

(5) Materials have large exciton energy for preventing the energy transfer of excitons, which are produced by charge recombination within an EML, to an ETL.

Adachi *et al.* (1989, 1990*a*) reported that 2-(4′-biphenyl)-5-(4″-tert-butylphenyl)-1,3,4-oxadiazole (t-Bu-PBD) was useful for an ETL and demonstrated the preparation of EL devices with the DL-H-type structure, especially blue EL devices. It turned out, however, that the stability of the vacuum-sublimed t-Bu-PBD thin-film was not enough for high performance devices (lack of condition (2.1)). In some cases, Alq, which is well known for being one of the best EML materials, can be used for the ETL. We have to note, however, that Alq does not always satisfy conditions (2.4) and (2.5).

Thus, new ETL materials were designed and synthesized based on the knowledge that t-Bu-PBD is one of the best ETL materials, except for the stability of vacuum-sublimed thin films (Hamada *et al.* 1992). An oxadiazole with dimer structure of t-Bu-PBD, named OXD-7, was found to be one of the best materials for ETL. The electron transporting tendency of OXD-7 was almost the same as that of t-Bu-PBD and emission maximum wavelengths, which can be used as measures of exciton energy, were located below 410 nm. Vacuum-sublimed thin films of OXD-7 gave uniform glassy films with higher softening temperatures than that of t-Bu-PBD. They were quite stable and no degradation due to spontaneous crystallization was found after 30 day-storage. Lately, we demonstrated that some oxadiazoles had excellent transporting capability by using a conventional time-of-flight method (Tokuhisa *et al.* 1995). Today, however, oxadiazoles are not considered to be very promising for electron injection and transport layers for multilayer EL devices due to high barriers for electron injection, even though the hole-blocking capability of oxadiazoles are excellent.

Varieties of organic dyes have been used for EML materials. A lot of fluorescent dyes with high quantum efficiency of fluorescence have been reported to be useful for the fabrication of high-efficiency EL devices. One should note that only a limited number of dyes are accepted to be robust materials, useful for EML, which show promise for applications. At present, we have no concrete answer why some emissive dyes are so tough compared with other hundreds of dyes tested. Some metal chelates such as Alq and related materials, Bebq (Hamada *et al.* 1993) and ZnPBO (Nakamura *et al.* 1994), have been reported to be useful. It should be noted that detailed molecular engineering is surely successful for obtaining emissive dyes with high EL efficiency and high durability. The success in the design of distyrylarylene derivatives such as DPVBi, for example, is a good illustration (Hosokawa *et al.* 1995).

Figure 4 shows the molecular structures of TPD, m-MTDATA, t-Bu-PBD, OXD-7, Alq, Bebq, ZnPBO and DPVBi.

4. Extension of molecular design concept to polymer-dispersed dye system

Charge transport and emissive dyes used for multilayer sublimed-dye EL can be utilized for charge transport and emissive dyes in polymer-dispersed dye EL. The roles of dyes as charge transport, charge recombination and emission in multilayer dye films and polymer-dispersed dye systems are almost the same. Figure 5 demonstrates an example of a polymer-dispersed dye system in which three kind of dyes, hole transport (TPD), electron transport (an oxadiazole derivative, BND) and emissive (coumarin-6) dyes, are dispersed in polymer matrices. The molecular structure of dyes used in these experiments are almost the same in the cases of sublimed-dye multilayer systems.

Two key points in designing polymer-dispersed dye systems are mentioned here. First, balance in charge injection and transport is adjustable by the change of the molar ratio of hole transport TPD and electron transport BND. The external quantum efficiency of 0.32% was attained in the device with the optimized TPD/BND composition. The second point is that emissive centres with high quantum efficiency of fluorescence are easily introduced in polymer-dispersed dye systems. Thus, we are free from the efforts in designing and synthesizing sophisticated molecules with both emissive and charge transporting capabilities.

We emphasize that both design and fabrication of polymer-dispersed dye systems are quite simple, but device performances of these simple single-layer devices are good. The EL performance of our optimized three-component device was comparable with conventional vacuum-sublimed multilayer-dye devices, except for high applied voltage values. The maximum luminence attained was about 1000 cd m^{-2} at current density of 170 mA cm^{-2} and applied voltage of 32 V (Lin *et al.* 1995).

Attainment of perfect balance and confinement of holes and electrons within emissive layers is not possible when a single-layer structure is used. No function for the blocking of charges is introduced in the single-layer polymer-dispersed system. Thus, the use of multilayer structures is expected to bring about further improvement in EL quantum efficiency even in polymer-dispersed dye systems. Actually, introduction of charge blocking layers contributed a drastic increase of EL quantum efficiency: insertion of an electron-blocking thin polyvinylcarbazole layer between ITO and the triple-component polymer-dispersed dye layer increased EL quantum efficiency to 1.2%. Furthermore, the insertion of a vacuum-sublimed dye OXD-7 hole blocking layer between a metal electrode and the triple-component dye layer resulted in an efficiency of 2.9%. These experiments clearly indicate that the use of multilayer structures are required even when every type of molecular material is introduced in EL devices (Lin *et al.* 1994).

5. Extension of molecular design concept to polymers with chromophores in skeletons

The usage of phrases such as 'hole and electron transport molecules' and 'emissive molecules' has been shown to be valid in polymer-dispersed dye systems. Thus, we expect that the molecular design concept on dye molecules is further extended to the chromophores incorporated in polymer chains. The validity of this idea was tested by directly comparing the EL performances of two different class of EL devices: one is made of vacuum-sublimed dye films and the other is made of solvent-cast polymer
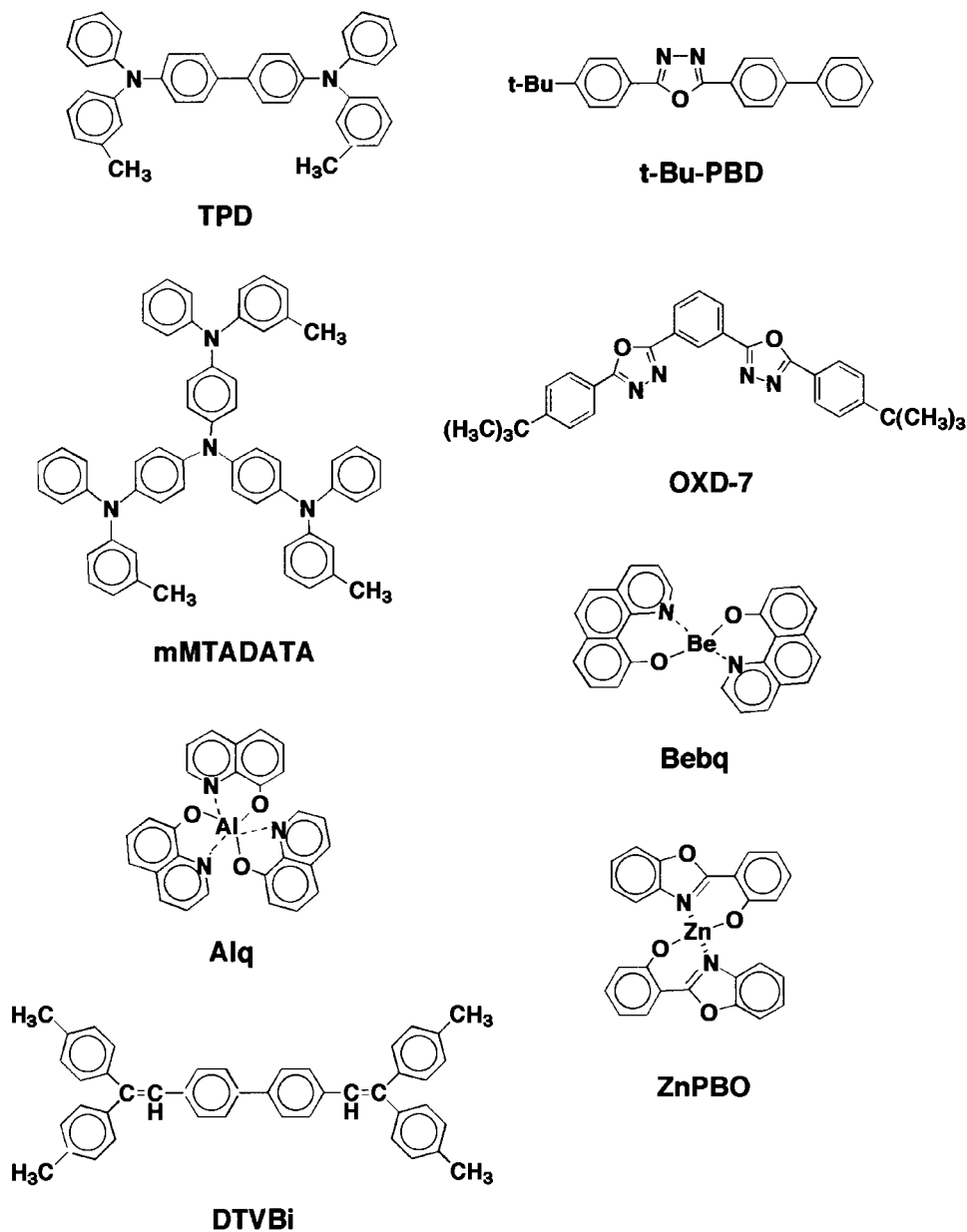
Figure 4. Molecular structures of dyes described in the text.

films. The most important issue to be stressed here is that we incorporate exactly the same functional group in both class of materials, even though both molar masses and methods of film-processing are quite different from each other (Kim *et al.* 1995*a*).

The chromophore used for this comparative study was a 9,10-bis[4-(N,N-diphenyl-amino)styryl]anthracene (BSA) group. A low molar mass dye, named dye-BSA, and a polymer in which the BSA chromophore is linked with an alkylether group, named polymer-BSA, were used (figure 6). In previous publications, we showed that dye-BSA exhibited excellent EL performance even in a single-layer device (Aminaka *et*
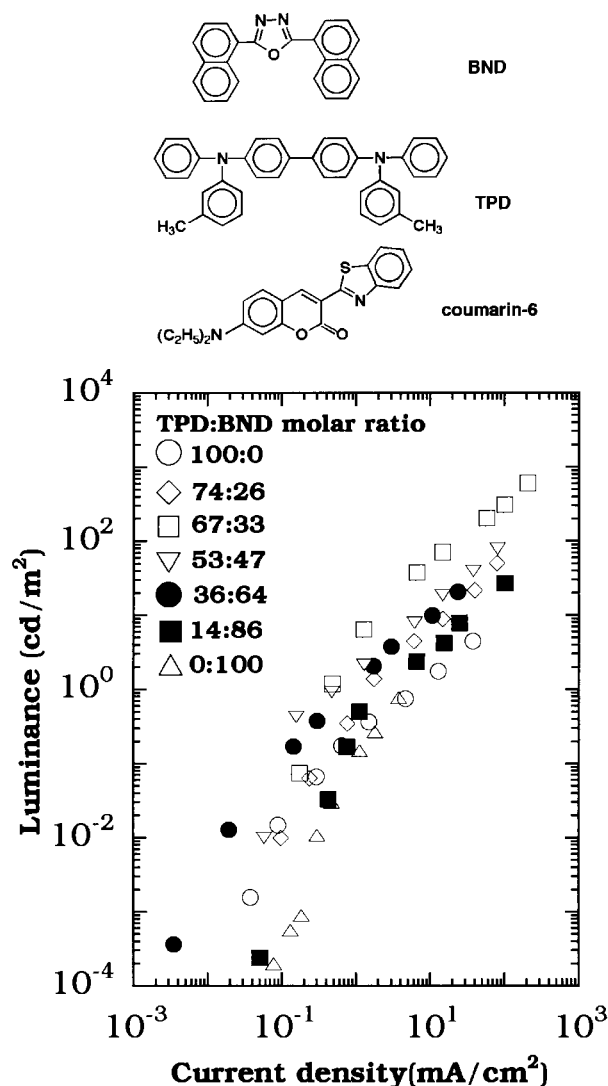
Figure 5. Luminence—current density relationships in triple-component single-layer devices. Molecular structures of TPD, BND and coumarin-6 are also shown. The content of binder polymer is 50 wt% and the TPD/BND molar ratios are indicated in the figure.

al. 1994). This fact makes it possible for us to directly compare the EL efficiencies between two devices made of dye-BSA and polymer-BSA. Because the BSA chromophore are assumed to have bipolar electronic properties with enriched hole transport ability, we also test the EL performance of double layer devices. Double-layer devices are fabricated by using OXD-7 dye as an electron transport layer.

Figure 7 shows the luminence–current density relationships in two single layer devices. In the dye-BSA device, luminence increased proportionally with the increase of current density, showing a typical behaviour on thin-film EL devices, and external quantum efficiency was calculated to be 0.018%. On the other hand, in the case of the polymer-BSA device, luminence was low at a small current density region and showed rapid increase at a high current density region, reaching the luminence level of
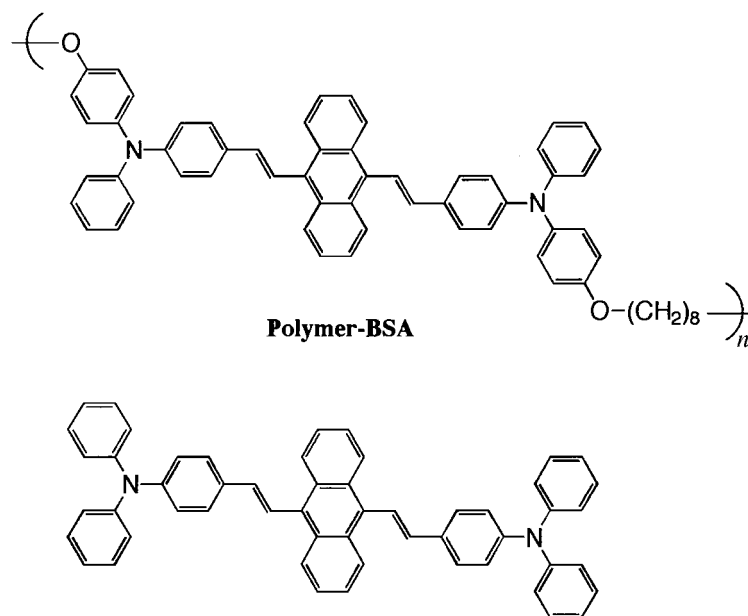
Figure 6. Molecular structures of BSA-based polymer and BSA dye.

the dye-BSA device. From the comparison of luminence–current density relationships between two devices, we found that the quantum efficiencies of dye-BSA device was about 7 times higher than that of polymer-BSA device at $250\,\mathrm{mA\,cm^{-2}}$. As we reported previously, dye-BSA has bipolar charge transport characteristics and exhibits high EL efficiency, even in the form of a single-layer device. These results therefore imply that the polymer-BSA film also show the same EL characteristics as the vacuum-sublimed dye-BSA film (if the film quality of polymer-BSA is high enough). When we use a double-layer structure, quantum efficiency is expected to increase and also the stability of devices may be improved. Figure 8 compares luminence–current density relationships in the double-layer polymer-BSA and dye-BSA devices. An increase of about 20 times the quantum efficiency was found in the case of the dye-BSA devices, when the OXD-7 layer was introduced due to the excellent hole blocking effect of the OXD-7 layer. In the case of the polymer-BSA devices, the double-layer structure was effective for the increase of stability of the devices at low applied voltage region. Nonlinearity in luminence–current density relationship was considerably improved in the double-layer polymer-BSA device. The EL characteristics on the polymer-BSA devices reported here demonstrates the importance of design of chromophores based on the experimental study on corresponding dye systems.

6. Concluding remarks

In this paper, we showed that EL efficiency is clearly defined based on simplified working mechanism of charge-injection-type electroluminescence of molecular materials. The balance of positive and negative charges injected and transported within thin films has a major contribution in determining overall quantum efficiency. Blocking of charges, by using charge blocking layers, further contributes to the increase in quantum efficiency. The molecular design concept of vacuum-sublimed dyes is based
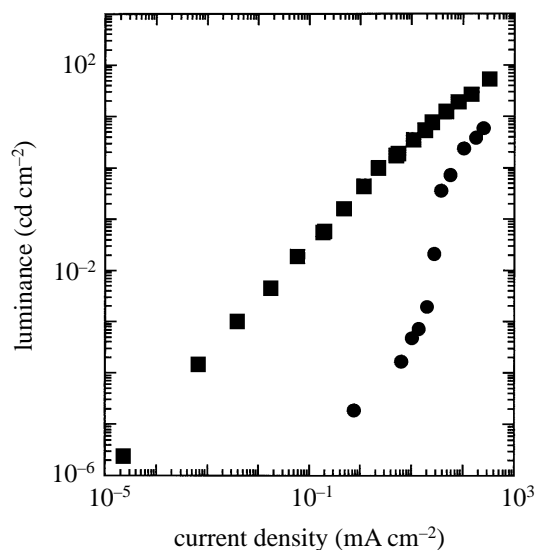
Figure 7. Luminence–current density relationships in single layer devices: ■, EL device made of vacuum-sublimed BSA dye; ●, EL device made of spin-coated polymer-BSA.
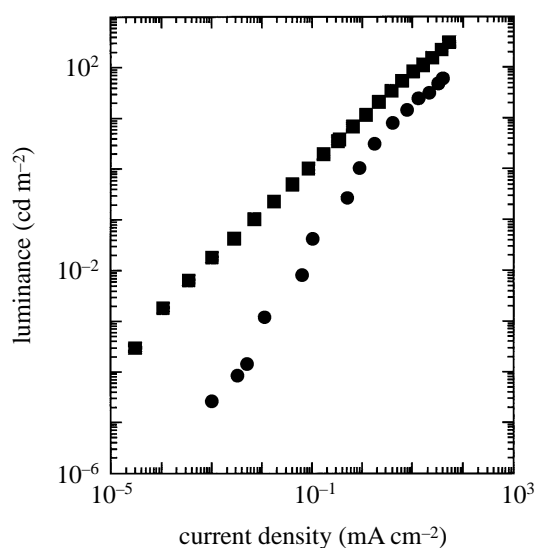

Figure 8. Luminence–current density relationships in double layer devices: ■, EL device made of vacuum-sublimed BSA-dye and OXD-7; ●, EL device made of spin-coated polymer-BSA and vacuum-sublimed OXD-7.

on these considerations and the concept can be extended to the cases of polymer-dispersed dye systems and polymers with chromophores.

Finally, we would like to stress that the use of the design concept of multilayer structure devices and molecular materials is quite helpful for the development in novel, unconventional EL devices such as EL devices with a molecular-size emissive layer (Era *et al.* 1991), microcavity EL devices (Tsutsui *et al.* 1994*c*), EL devices with polarized emission (Era *et al.* 1995) and multilayer EL devices with a layered perovskite emissive layer (Era *et al.* 1994).

References

Adachi, C., Tsutsui, T. & Saito, S. 1989 Organic electroluminescent device having a hole conductor as an emitting layer. *Appl. Phys. Lett.* **55**, 1489–1491.

Adachi, C., Tsutsui, T. & Saito, S. 1990*a* Blue light-emitting organic electroluminescent devices. *Appl. Phys. Lett.* **56**, 799–801.

Adachi, C., Tsutsui, T. & Saito, S. 1990*b* Confinement of charge carriers and molecular excitons within 5 nm-thick emitter layer in organic electroluminescent devices with a double heterostructure. *Appl. Phys. Lett.* **57**, 531–533.

Aminaka, E., Tsutsui, T. & Saito, S. 1994 Electroluminescent behaviors in multilayer thin-film electroluminescent devices using 9,10-bisstyrylanthracene derivatives. *Jap. J. Appl. Phys.* **33**, 1061–1068.

Aminaka, E., Tsutsui, T. & Saito, S. 1996 Effect of layered structures on the location of emissive regions in organic electroluminescent devices. *J. Appl. Phys.* **79**, 8808–8815.

Era, M., Adachi, C., Tsutsui, T. & Saito, S. 1991 Double-heterostructure electroluminescent device with cyanine-dye bimolecular layer as an emitter. *Chem. Phys. Lett.* **178**, 488–490.

Era, M., Morimoto, S., Tsutsui, T. & Saito, S. 1994 Organic-inorganic heterostructure electroluminescent device using a layered perovskite semiconductor $(C_6H_5C_2H_4NH_3)_2PbI_4$. *Appl. Phys. Lett.* **65**, 676–678.

Era, M., Tsutsui, T. & Saito, S. 1995 Polarized electroluminescence from oriented p-sexiphenyl vacuum-deposited film. *Appl. Phys. Lett.* **67**, 2436–2438.

Hamada, Y., Adachi, C., Tsutsui, T. & Saito, S. 1992 Blue-light-emitting organic electroluminescent devices with oxadiazole dimer dyes as an emitter. *Jap. J. Appl. Phys.* **31**, 1812–1816.

Hamada, Y., Sano, T., Fujita, M., Fujii, T., Nishio, Y. & Shibata, K. 1993 High luminescence in organic electroluminescent devices with bis(10-hydroxybenzo[h]quinolirato)beryllium as an emitter. *Chem. Lett.* 905–906.

Helfrich, W. & Schneider, W. G. 1966 Transients of volume-controlled current and recombination radiation in anthracene. *J. Chem. Phys.* **44**, 2902–2909.

Hosokawa, C., Higashi, H., Nakamura, H. & Kusumoto, T. 1995 Highly efficient blue electroluminescence from a distyrylarylene emitting layer with a new dopant. *Appl. Phys. Lett.* **67**, 3853–3855.

Kim, D. U., Aminaka, E., Tsutsui, T. & Saito, S. 1995*a* Comparison of device performance in two thin-film electroluminescent devices made of vacuum-sublimed dye film and spin-coated polymer film. *Jap. J. Appl. Phys.* **34**, 6255–6259.

Kim, D. U., Tsutsui, T. & Saito, S. 1995*b* Design and synthesis of processable electroluminescent polymer with charge transport capability. *Polymer* **36**, 2481–2483.

Lin, C. P., Tsutsui, T. & Saito, S. 1995*a* Emission characteristics of electroluminescent devices using molecularly-doped polymer films. *New Polymeric Materials* **4**, 277–288.

Lin, C. P., Tsutsui, T. & Saito, S. 1995*b* The effect of charge blocking layers in electroluminescent devices made of molecularly-doped polymer films. *J. Chem. Soc. Jap.* (in Japanese) 649–655.

Nakamura, N., Wakabayashi, S., Miyairi, K. & Fujii, T. 1994 A novel blue light emitting material prepared from 2-(o-hydroxyphenyl)benzoxazole. *Chem. Lett.* 1741–1742.

Pope, M & Swenberg, C. E. 1982 *Electronic processes in organic crystals.* New York: Clarendon.

Shirota, Y, Kuwabara, Y., Inada, H., Wakimoto, T., Nakada, H., Yonemoto, Y., Kawami, S. & Imai, K. 1994 Multilayered organic electroluminescent device using a novel straburst molecule as a hole transport material. *Appl. Phys. Lett.* **65**, 807–809.

Tokito, S., Tsutsui, T., Saito, S. & Tanaka, R. 1986 Optical and electrical properties of pristine poly(p-phenylenevinylene) film. *Polymer Commun.* **27**, 333–336.

Tokuhisa, H., Era, M., Tsutsui, T. & Saito, S. 1995 Electron drift mobility of oxadiazole derivatives doped in polycarbonate. *Appl. Phys. Lett.* **66**, 3433–3435.

Tsutsui, T. & Kim, D. U. 1996 Material design of polymers with chromophores in skeletons for electroluminescent devices. *Mol. Cryst. Liq. Cryst.* **280**, 319–324.

Tsutsui, T. & Saito, S. 1993 Organic multilayer-dye electroluminescent diodes—is there any difference with polymer LED? In *Intrinsically conducting polymer: an emerging technology* (ed. M. Aldissi), pp. 123–134. Dordrecht: Kluwer.

Tsutsui, T., Aminaka, E., Hamada, Y., Adachi, C. & Saito, S. 1993 Significance of multilayer structures in organic thin-film electroluminescent devices. *SPIE Proc.* **1910**, 180–189.

Tsutsui, T., Aminaka, E., Lin, C. P. & Saito, S. 1994a Progress in material design for organic electroluminescence. In *Proc. 1994 Int. Workshop on Electroluminescence* (ed. X. Xu), pp. 135–144. Beijing: Science.

Tsutsui, T., Lin, C. P. & Saito, S. 1994b Charge injection, transport, recombinations and generation of neutral excitations in multilayer-dye electroluminescent diodes. *Mol. Cryst. Liq. Cryst.* **256**, 63–70.

Tsutsui, T., Takada, N., Saito, S. & Ogino, E. 1994c Sharply directed emission in organic electroluminescent diodes with an optical-microcavity structure. *Appl. Phys. Lett.* **65**, 1868–1870.

Discussion

Xiao-Chang Li (*Chemistry Department, University of Cambridge, UK*). (1) In relation to the cromatic oxadiazole, the aromatic oxadiazole can play an electron transporting role and a hole blocking role. Which role does Professor Tsutsui think dominates most?

(2) The electroluminescence efficiency is governed by three factors, i.e. charge injection factor, factor of singlet production and the material's fluorescence effeciency. You state that each factor can approach unity. Does this mean that the EL efficiency can also theoretically achieve unity?

T. Tsutsui. (1) The hole blocking role of oxadiazoles are very important, because the electronic affinity value of aromatic oxadiaxoles is small and not good for electron injection from metal cathodes. However, I would like to add the comment that the aromatic oxadiaxoles have very good electron transport capability.

(2) The charge injection factor can be very close to unity by using appropriate multilayer device structures. The maximum value of the factors of singlet exciton production is believed to be 0.4, due to spin statistics at charge recombinations. The fluorescence quantum efficiency can be very close to unity by choosing the dyes or chromophores to have sufficiently high quantum efficiency of photoluminescence. Note that external quantum efficiencies are about a fifth of internal quantum efficiencies.

I. Sage (*DRA Malvern, Malvern, UK*). A lesson learned in the early stages of the development of liquid crystal displays, is that very high levels of purity are needed in these organic materials in order to achieve good operating lifetime in devices. What are th epurity levels of the materials used for fabrication of organic EL devices, and how are they achieved and measured?

T. Tsutsui. The dye materials used in these devices are purified by vacuum sublimation before use, but the polymers are used without any special purification steps. The actual purity of the deposited films is not known.

A. Vecht (*School of Chemical and Life Sciences, University of Greenwich, UK*). What are the effects of the introduction of rare earths into molecular electronic materials? Would Professor Tsutsui expect any energy transfer from the organic materials to the rare earth to yield improved light emission?

T. Tsutsui. Several researchers have already reported the use of rare earth metal chelates for emissive materials. It appears that the charge recombinations occur

814   *T. Tsutsui, E. Aminaka, C. P. Lin and D.-U. Kim*

on legand molecules and excited energy is effectively transferred to inner rare earth cations. Because the energy transfer process includes a triplet–triplet energy transfer, it is expected that triplet states, which are directly produced via charge recombinations on legands, may be used for excitation of inner rare earth cations. Thus, the increase of the overall efficiency of production of final emissive species is expected. Howvere, no reported experimental results have proved these points as yet.