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RECENT DEVELOPMENTS IN MOLECULAR ORGANIC ELECTROLUMINESCENT MATERIALS

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Abstract: A review of recent developments in the design and use of small molecular organic electroluminescent materials for display applications is presented. The material issues pertaining to transport properties, color, emission efficiencies, and operational stability are described.

1. Introduction

Since the discovery of a thin-film organic electroluminescent device by the team at Kodak,[1] there have been many interests and research activities driven by this new organic light emitting diode (OLED) technology. The colors and high luminescence coupled with low driving voltage of organic EL devices are particularly suited for applications in flat panel displays. This review is written primarily from an organic chemist's point of view. It is intended to focus on the design of organic materials with novel structures used in EL devices that have been disclosed in the scientific papers and patent literatures from 1990 through the early part of 1997. For earlier developments in this field, the readers can consult a review article published by Kido[2]. We will limit our discussions to the most significant discoveries and advances made in the area of "small molecular" organic EL materials, which can be vacuum deposited as thin films. Polymeric electroluminescent materials, which were first demonstrated in 1990,[3] have been reviewed elsewhere.[4,5] The device principles, applications requirements and reliability issues of organic electroluminescent devices have also been discussed recently.[6]

Electroluminescence (EL) is a subject of long-standing interest because of its technological importance.[7] It has been described as a phenomenon of generating "cold" light. Generally, EL devices can be classified into two types: the light emitting diode (LED) from Group III-V semiconductors and the thin-film electroluminescent

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panel (TFEL) from Group II-VI materials, primarily ZnS. LED is a low-voltage high-current injection device with light generation caused by the radiative recombination of charge carriers injected over a P-N junction. TFEL is a high-voltage, low-current avalanche device where light is produced by a high-field impact excitation process. Both types of device are well developed and have found wide-spread applications in optoelectronics and displays. However, despite decades of continuing development, there are still major deficiencies. The efficiency of these EL light sources remains relatively poor in comparison with an ordinary incandescent light bulb. LED, based on a single-crystal substrate, is generally limited to small discrete elements. TFEL is slow in temporal response and requires a high AC voltage of several hundred volts. Color is also a major issue. Blue EL emitters are rare and inefficient. The lack of blue emitters has, in effect, prevented the development of full-color EL display panels thus far.[8]

Faced with rapid advances in other display technologies, notably in liquid crystal and plasma displays, and lured by the potentially huge demand for full-color flat panel displays in the marketplace, there is a great deal of competitive pressure as well as incentive to further the development of EL technology. Interest in electroluminescence has prompted the intense development of organic EL in recent years. As we will describe in this review, organic materials provide a promising medium for EL devices.

1.1 Organic Materials

A key reason for choosing organic materials is the high fluorescence efficiency characteristic of many organic molecules. In particular, intense blue fluorescence with near unity quantum yield is known to exist in many classes of organic compounds. Stilbenes, coumarins, and anthracenes are a few examples. In fact, early work on organic electroluminescence in anthracene crystals has shown an efficiency as high as 5% in emitted photons per injected carrier. The theoretical maximum is about 25%, limited only by the probability of creating radiative singlets in the electron-hole recombination process.[9]

For EL applications, the high fluorescent efficiency of organic materials is, however, greatly compromised by their insulating nature. In effect, the luminance achievable from organic EL devices can be severely limited by the low level of current that can be injected into the insulator at a given electrical field. For general display applications, an adequate brightness under ambient viewing conditions is about 100 cd/m^2. The minimum EL current may therefore be defined as one which would produce at least this level of luminance. This means that for a diffuse or Lambertian EL emitter having a modest external quantum efficiency of, say, 1%, the steady-state EL current needed is on the order of 1 mA/cm^2. For an organic insulator, this is a fairly large current. To make matters much worse, this current level would have to be increased by two or three orders of magnitude in a display panel using a time-multiplexed addressing scheme. Thus, for organic materials to be useful, it is absolutely necessary to overcome this injection current limitation. The approach, therefore, calls for novel EL structures.

1.2 Injection Contacts

In the simplest configuration, the EL device may consist of a luminescent organic solid sandwiched between a pair of injecting electrodes. Assuming that both the cathode and anode are perfectly injecting, the current through the EL device would be ultimately limited by the space charges injected into the organic insulator. This "space-charge-limited" (SCL) current can be estimated for an idealized or trap-free, single-carrier organic system. For a prototypical organic crystal with a carrier mobility of 1 cm^2/V/s and a dielectric constant of *3*, the maximum SCL current that can be drawn through a crystal at an applied voltage of 100 Volts is only a few microAmperes. This current is many orders of magnitude too small to be useful even for the most efficient EL material. Thus, one can easily rule out the use of single crystalline organic solids for practical EL applications. The early work, particularly those by Helfrich and Schneider[10] on anthracene crystals, nevertheless, provided the general groundwork for understanding organic electroluminescence.

Obviously, it is important to use thin structures for organic EL devices. In fact, from deliberately thinned crystals to evaporated or spin coated organic thin films, EL devices spanning a thickness from tens to tenths of microns have been explored with various degree of success. In particular, using ultrathin films, the SCL current limit may be pushed to a level which is too high to be reachable and therefore irrelevent under ordinary EL drive condition. For instance, with a carrier mobility value as low as 1E-5 cm^2/V/s, which is as much as five orders of magnitude below that in single crystal organics and which is not at all uncommon in disordered organic systems, the SCL current through a 0.1 micron film is about a few tenths of an

Ampere/cm^2 at a low bias of 10 Volts. This current level is sufficient for most EL applications requiring a modest multiplexing scheme.

Whereas the SCL transport mechanism might place an ultimate upper limit for the drive current, it is often one or both of the electrical contacts which in practice limits the current through the organic EL structure. Very often it is the cathode or electron injecting contact that poses the most serious problem, because it requires a low work function metal such as an alkaline metal, which by nature is highly reactive. For thin-film EL devices, evaporated metal films are generally used for the electron injecting contact, mainly because they can be applied in a controlled atmosphere onto a large area. It was discovered that evaporated Mg alloyed with a small amount of silver is an excellent choice. Mg is a relatively stable metal with a work function of 3.5 eV which is sufficiently low for it to be useful as an electron injecting electrode. The small amount of Ag assists the Mg deposition by presumably providing nucleating sites on the alloyed film during co-deposition. Other more reactive alkaline earth metals such as Ca has also been found to be useful in connection with polymer EL films, such as polyphenylvinylene.[11] A Li:Al alloy was recently used to lower the driving voltage of organic EL devices.[12]

In the recent *SID 97 Meeting*, Kido[13] described a novel "metal-doped electron-injecting layer". The idea is that the organic layer at the cathode interface is doped with a low-work function metal, such as Li, so that organic molecules are reduced to form radical anions. Therefore the barrier height for electron injection from the cathode to the organic layer may be reduced. Thus, it was stated that the work function of the cathode material may no longer be critical. In a device structure of **[ITO/NPB/AlQ$_3$/Li-doped AlQ$_3$/Al]**, a high luminance of over 30,000 cd/m^2 was achieved compared to only 6,700 cd/m^2 without the Li-doped AlQ$_3$ electron-injecting layer.

The hole injecting contact requires a metal of high work function to match with the valence band level of the organic material. The choice is much easier since most of these metals, such as Au, are inert. The most commonly used electrode is a conducting metal oxide such as indium tin oxide with a work function of about 4.5-5.3 eV depending on the methods of measurement.[14] It is reasonably inert, highly conductive (electrically) and optically transmissive.

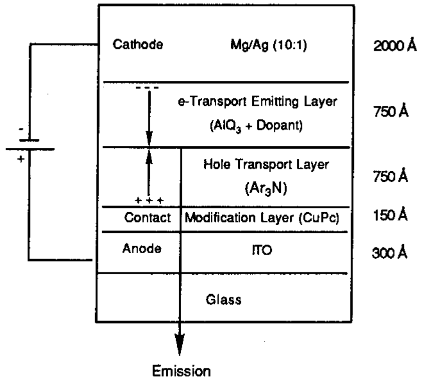
Neither the cathode nor the anode is believed to be sufficiently injecting at the high current level required by EL devices. From a direct measurement of the photo-ionization potential of the organic thin films or an indirect measurement of the redox potential in solutions, potential barriers as high as a few tenths to one eV are known to occur at the contacts. Barriers of such a magnitude are also revealed in the analysis of current-voltage measurements of the actual EL device. It is the lowering of the barrier height or the narrowing of the barrier width with an applied electric field that causes the carrier to escape or tunnel from the electrode to the organic medium.

1.3 Electron-Hole Recombination and Multilayer Structure

Once the electron and hole injecting contacts are functional, the next task is concerned with manipulating the electron-hole recombination in such a manner that nonradiative decay paths can be minimized. With an ultrathin film, it is a delicate matter of balancing the carrier injection and recombination processes. One of the major quenching sites lies in the contacts themselves. Therefore, it is important to design an EL structure that has carrier recombination occurring away from the contacts. For a thick, single crystal such as anthracene where both electrons and holes are relatively mobile, the recombination zone is mostly in the bulk. Thus, the electrode contacts quenching pathway is apparently unimportant and the EL yield is found to be rather high, reportedly about 5% photons/electron. Control of the carrier recombinaton zone in thin-film EL devices is, however, much less well characterized.

For reasons that are not entirely understood, most organic thin films support preferentially the transport of either electrons or holes, but not both to any equal extent. Thus, the use of these unipolar films favors the localization of the recombination zone at either the cathode or anode interface, depending on whether the hole or the electron is the more mobile species. In either case, the EL efficiency will be greatly reduced because the excited states generated at or near one of the contacts are largely quenched by the metallic surface. One obvious solution to this problem is to deliberately modify an organic thin film to give it a bipolar transport property. This can be done by using multi-component films having an appropriate mix of hole and electron transport molecules. A simpler and more useful method employs a bilayer structure comprising a hole transport layer and an electron transport layer, with one or both layers being luminescent. We have extensively explored this bilayer structure and have produced extraordinarily bright EL devices with a high efficiency.[15] Remarkably, this is achieved using a drive voltage of no more than 10 Volts. More refined device structures include additional layers such as the luminescent layer between the hole-transport layer and eletron-transport layers which improves the emission characteristics, as well as a contact modification layer, such as copper phthalocyanine, which improves the hole injection from the anode into the EL layers. **Figure 1** shows a prototype device with a multilayer EL structure using an aromatic diamine as the hole transport layer and *tris*(8-hydroxy-quinolinato) aluminum (AlQ_3) plus dopant as the electron transport emitting layer.

Fig. 1. Kodak's Multilayer Structure of a Thin-Film EL Device



Using this multilayer structure and several other variations, we have shown that the electron-hole pair recombination can be largely confined to the interface between the two organic layers. By spacing this interface at a sufficient distance from the contacts, the probability of quenching near the metallic surfaces is greatly reduced. As a result, the EL emission is highly efficient. To some extent, each organic layer in this bilayer structure can be independently optimized with respect to its carrier transport and luminescent properties, providing a considerable degree of freedom in the choice of organic materials for EL devices. In fact, numerous organic materials have since been investigated in various multilayer structures, adopting the basic bilayer principle.

1.4 Color

Recombination electroluminescence in a molecular solid has a maximum quantum yield of 25% (photon/electron), ignoring the contribution of triplet states. With other losses, such as that due to optical coupling, an overall yield of 5% should be achievable from organic EL devices throughout the visible region. Assuming this 5% quantum yield, a 5 V drive, and a set of blue, green, and red emission bands with an arbitrary Gaussian shape, the luminous charateristics can be derived, as listed in **Table 1.**[16] These values indicate that broadband emitters like organic ELs with a bandwidth of about 75-100 nm can produce a color gamut reasonably matched to the *CRT.* Also, it can be seen that extremely high luminance efficiencies can be realized from these emitters if they can be driven with a sufficiently low voltage.

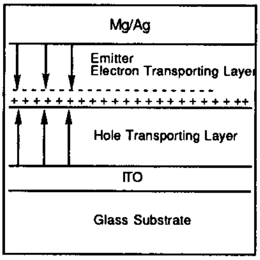
Table 1. EL Characteristics Derived From Gaussian Emission Bands (FWHM = 75nm) And A 5% Photon/Electron Quantum Yield

EL Color	Blue	Green	Red
Peak Wavelength (nm)	460	535	620
CIE-x	0.137	0.269	0.624
CIE-y	0.084	0.628	0.374
Lum. eff. (cd/A)	3.47	18.8	9.1
Lum. eff. @ 5V(lm/W)	2.2	12.0	5.7

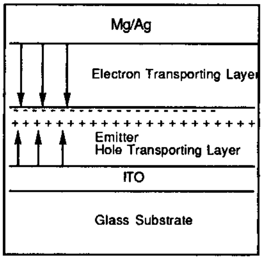
The AlQ_3 layer in the multilayer structure described above is responsible for the broadband green EL emission, peaking at about 530 nm. Other EL colors can, in principle, be obtained by choosing different organic fluorescent materials as emitters. Indeed, numerous fluorescent molecules have been found, or newly designed, to produce EL emissions of other hues. Another method for tuning the EL colors is by doping into a host material, such as AlQ_3, a small amount of specific guest molecules.[17] By direct excitation or via energy transfer from the host, the guest molecule emits with its characteristic luminescence. In addition to tuning the EL colors, this scheme provides a means of enhancing the overall EL efficiency by fully capitalizing on the strong fluorescence of the guest. For a doped AlQ_3 system, a greater than threefold increase in efficiency has been realized over the undoped system. Other methods for tuning the EL spectra may include optical interference effects involving the dielectric and metallic thin films in the EL structure.

2. Cell Configurations

In order to discuss the various materials used in a EL device, it is necessary to briefly describe the corresponding cell configurations published to date. There are four basic types of EL cell configurations for the vacuum deposited molecular device. The most widely used is the dual-layered format shown in DL-A.[1] The key component of this device is the emitter layer that is also electron-transporting. A typical cell is sequentially composed of a glass support/ITO/hole transport layer/emitter (electron transport) layer/Mg:Ag. A group of researchers at Kyushu University[18] demonstrated that it was also possible to mimic the configuration by using emitters that have hole-transporting properties as shown in **DL-B**. In this device, the emission would come from the entire hole-transporting layer as the *exciton* generated by carrier-recombination at or near the interface is known to diffuse throughout much like the cell configuration **DL-A**.

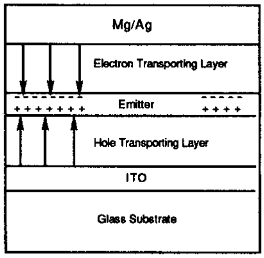


DL-A

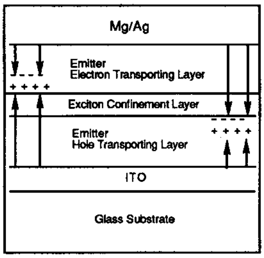


DL-B

This group later also published a triple-layered type device as sketched in TL-C. A typical structure is composed of a glass support/ITO/hole transport layer/emitter/electron transport layer/Mg:Ag. The emitter layer could be as thin as a Langmuir-Blodgett film of bilayer of an organic dye and still be capable of confining the excitons generated in the bilayer to emit intense luminescence.[19] Kido[20] modified the triple-layered structure into what he termed a "confinement structure" as sketched in TL-D. Depending on the thickness of the "exciton confinement layer", it is possible to electroluminesce either from the ET or HT layer. If the "confinement layer" is properly constructed, it is possible to observe the emissions from both layers, which allows them to generate white light by mixing.[21]



TL-C



TL-D

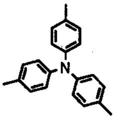
There are also single-layered devices which were particularly suitable for polymer films containing both ET and HT materials or materials with bipolar properties.[11] These devices will not be discussed in this report.

3. Hole Transport Materials

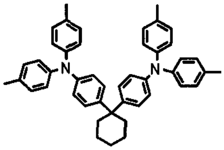
Numerous materials have been developed for the hole transport layer (HTL) in organic EL devices. Most of these hole transport materials, which were developed for charge transport layers in xerography, are arylamine derivatives.[22,23,24] These arylamine derivatives with high hole drift mobilities (on the order of 10^{-3} cm/Vs for xerography) were designed mainly for use in copy products where they were mixed with a suitable polymeric binder and solvent-coated as a charge transport layer in a photoconductive system. However, in addition to high mobility, the hole transport material used in thin film organic EL devices must also be able to generate a pinhole free thin film by vacuum evaporation.

In early studies, researchers at Kodak[25] demonstrated that *N,N,N-tris*(*p*-tolyl)amine (HTM1) and 1,1-*bis*[(di-4-tolylamino)phenyl]cyclohexane (HTM2) are useful hole transport materials for EL devices. In practice, HTM2 is better than HTM1 because it has a higher vaporization temperature which is more suitable for thin film formation by vacuum evaporation.

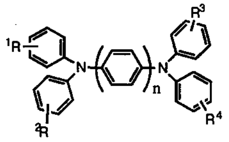
Later, it was found that using *tri*-arylamines with general structure I as the hole transport layer greatly improved both EL efficiency and operational stability.[26]



HTM1

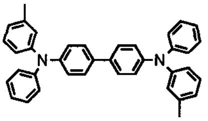


HTM2

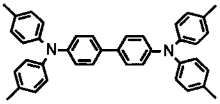


I

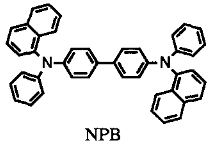
These *tri*-arylamine derivatives include most of the important hole transport materials, such as *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)(1,1'-biphenyl)4,4'-diamine (TPD), *N,N,N',N'-tetrakis*(4-methylphenyl)(1,1'-biphenyl)-4,4'-diamine (TTB), and N,N'-bis-(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB), which are widely used in current organic EL research.



TPD



TTB

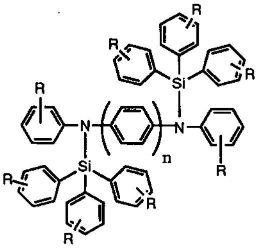


NPB

Studies on the design and synthesis of new hole transport materials for organic EL applications were mainly focused on finding materials with high thermal stability, a small energy barrier at the interface of an HTL/anode, and an ease to form good morphology as thin films.

The propensity of hole transport material to crystallize on aging is thought to be one of the main causes of degradation of organic LED's.[27] For example, after TPD thin film is prepared on indium-tin-oxide (ITO) substrate by the vapor-deposition method, the crystallization of TPD can be observed after a few hours (at 25 °C in air). Later, it was *found[28] that crystallization of TPD thin film could be succcessfully suppressed by* plasma modification. However, the EL efficiency of the organic LED with a plasma-modified hole transport layer was lower than that of the conventional organic LEDs and the lifetime of the organic LED could not be improved.

Silanamine compounds used as the hole transport material were found to defer recrystallization.[29] The conditions to improve the device durability, however, were not disclosed.. Their ionization potentials are similar to that of TPD (from 5.5 eV to 5.7 eV). It indicated that replacing the two phenyl groups of TPD with two triphenylsilyl groups may improve the amorphous properies, but did not seem to affect their electronic properties very much.



n = 1, 2, 3.
R = alkyl, aryl, and fused aryl

Investigation of the relationship between thermodynamic parameters and amorphous properties of hole transport materials suggested that heat-resistive and stable nonpolymeric organic dye (include hole transport materials) glasses can be formed from large, symmetrical, globular, rigid, and dense molecules with weak intermolecular cohesion.[30] Certain structure-activity relationships between amorphous properties and thermodynamic parameters of hole-transport materials have been established and rationalized theoretically. According to these findings, it was revealed that high glass transition temperatures (T_g), maximum crystal-growth temperatures ($T_c$max) and a minimum crystal-growth velocity (MCV) yielded the most stable organic glasses with high thermal stability.

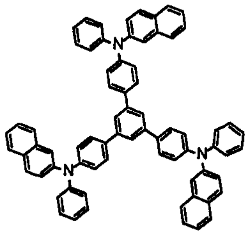
The hole transport materials used in EL devices which have a glass transition temperature somewhere below 100 °C are compared in **Table 2.**

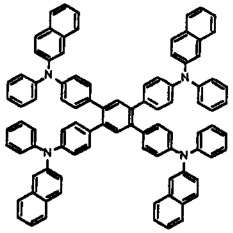
Table 2. T_g of Commonly Used Hole-Transport Materials

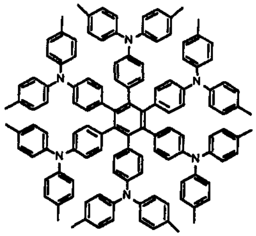
HTM	T_g°C
TPD	60
HTM2	78
TTB	82
NPB	98

In comparison, the electron transporting material currently used in most EL devices, AlQ_3, has a glass transition temperature of 175 °C. It is clear that the hole transport layer represents the weakest link in the entire EL structure considering the thermal stability of the materials. Therefore, the thermal integrity of these films should be one of the most critical factors in cell fabrication.

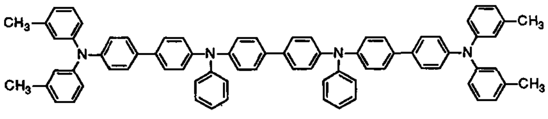
An important aspect that affects the performance of the organic EL devices is the morphological stability of the organic thin film layers. The transition of an organic thin film from an amorphous state to a crystalline or semi-crystalline state, or from one crystalline state to another, can result in a physical or morphological change in the thin film. This transition is generally dependent on temperature. In principle, all the organic layers forming the EL device should have as high a glass transition temperature as possible and the individual layer that has the lowest Tg is likely to be the one that would limit the overall stability of the EL device. A series of aromatic amines, which are useful hole transport materials for the organic EL devices, with glass transition temperatures as high as 165° C have been disclosed recently.[31]





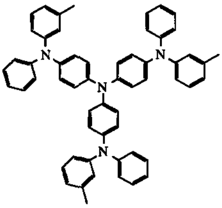


Oligomeric triphenylamines have been used in organic electroluminescent devices as the high heat-resistive and amorporous hole transport materials.[32] One noted example is TPTE. It has a high T_g of 130° C and also forms a uniform amorphous thin film by conventional vacuum deposition. Thermally stable EL devices fabricated using the basic configuration of [Mg:Ag/TPTE (700 Å)/AlQ3 (700 Å)/ITO] have been shown to operate continuously up to 140° C without breakdown.[33] In addition, a lowering of turn-on voltage to 2.1 V for light emission and an increase of luminous efficiency up to 1.25 lm/W with increasing temperature are reported at 130° C.



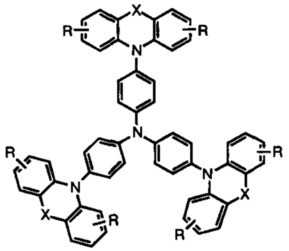
TPTE

A novel π-conjugated *starburst* molecule 4,4',4"-*tris*(3-methylphenylphenylamino)triphenylamine (*m*-MTDATA), which forms a stable amorphous glass and functions as an excellent hole transport material, was reported by Shirota[34] and Pioneer Electronic Corporation.[35] Some of the glass transition temperatures of the glassy thin film of the starburst aryl amines are reported to be higher than 200 °C.



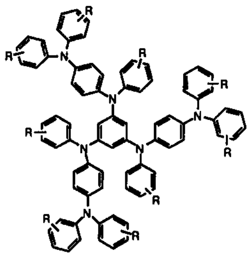
m-MTDATA

The hole transport layer, which is made of *tris*-(phenothiazinyl)-triphenylamine or *tris*-(phenoxazinyl)-triphenylamine derivatives, has both high heat-resistant properties and conductivity which improves durability. It emits at both high luminescence and efficiency upon application of a low voltage.[36]



(X = S, O; R = alkyl)

Other "starbust" triphenylamine derivatives used in organic EL devices as hole transport materials, such as the general structure shown below, were also reported.[37]



Ionization potential (I_p) of hole transport layers (HTLs) is a dominant factor in the molecular design approach of hole transport materials for producing high durability EL devices.[38] In particular, the formation of the small energy barrier at the interface of a HTL/anode is required for high durability. An electronluminescent device consisting of a double hole transport layer of *m*-MTDATA,TPD and an emitting layer of AlQ_3 exhibits a high-luminance efficiency and significant durability. This improved performance could be rationalized by the low solid-state ionization potential (Ip) of this class of hole transport materials as sketched in **Figure 2.**

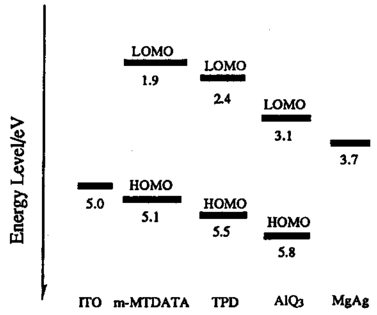
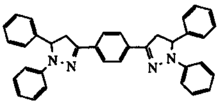
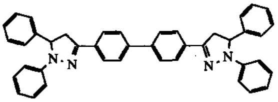


Fig. 2. Energy Levels of Electrodes and Organic Materials

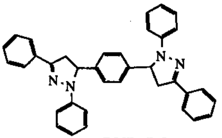
Dimer structures of pyrazoline derivatives were synthesized to obtain stable films and applied to electroluminescent (EL) devices as hole transport materials.[39] When pyrazoline dimer (PYR-D2) and AlQ_3 were used as HTL and EML (emitting layer) respectively, the EL device showed a maximum luminance of 12,400 cd/m^2 at 11 V and a maximum luminous efficiency of 1.5 lm/W at 250 cd/m^2. Pyrazoline dimers (PYR-D3) functioned just as well.



PYR-D1



PYR-D2



PYR-D3

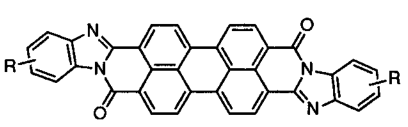
Quinacridone (QA), which was used by the Pioneer group as a very efficient green dopant (see Section 6.1), has also been shown to transport holes. Its vacuum deposited film gives a uniform thin film with a very fine polycrystalline texture. The thermal stability of the quinacridone film is found to be almost the same as that of AlQ_3, whose melting temperature is around 350 °C.[40]

Finally, one can not leave this section without mentioning some of the recent work involving the use of *polymeric* and molecularly doped polymers (MDP) as hole-transport materials in OEL device fabriation. One of the causes of degradation of an evaporated multilayered cell is believed to be the recurring crystallization of organic layers caused by heat produced in the cell.[41] In this case, the contact between each layer, including the hole-transport layer, may be destroyed by the crystallization of the vacuum deposited molecules. Therefore, employment of less crystalline polymeric materials may improve the lifetime of the devices, and single-layer-type devices rather than multilayer-type devices may achieve an improvement of structural stability. Recently, double-layered EL devices with a polymeric hole transport layer[42] and single-layered devices with intrinsically conductive polymers have been reported.[43] Kido demonstrated one of the most efficient EL devices using a TPD doped polycarbonate system as a hole transport layer. A bright green emission from the AlQ_3 layer with luminance of 7,700 cd/m^2 was observed at a driving voltage of 16 V.[44]

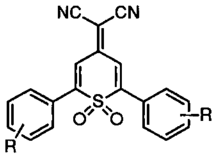
4. Electron Transport Materials

Most electron transport materials are used as host emitters as well and will be discussed fully in Section 5.1. When a hole transport layer or dopant emitting layer is used as the emitting layer, an electron transport layer is necessitated to carry the electron from the cathode to the emitting layer.

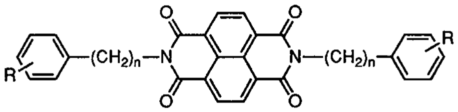
The most important electron transport materials are metal chelates such as AlQ$_3$, and BeBq$_2$, 1,3,4-oxidiazole derivatives (OXDs) such as PBD, and 1,2, 4-triazoles (TAZs). Nevertheless, other ET materials such as the *bis*(benzimidazolyl) derivatives of perylenedicarboximide (PD), naphthalenedicarboximide (ND)[45] and thiopyran sulfones (TPS),[46, 47] have been used in organic EL devices.



PD



TPS



PD

5. Host Emitter Materials

Among the OEL materials that have been reported, there are basically two types of emitter layers used in the devices. The most commonly employed emitter layer is one requiring organic molecules that possess both the properties of carrier-transporting and luminescence. In this report, it is called the **host emitter.** Dependent upon the cell configuration, the host emitter layer can be either *electron-transporting* or *hole-transporting.* Some of the materials have also been shown to be bipolar. This type of emitter is often employed in conjunction with a separate charge-carrier layer to confine and maximize charge recombination at, or near, the interface.

The other type of emitter is often referred to as the **dopants**, which is generally dispersed in the host matrix by coevaporation. The dopant molecules are organic fluorescent dyes, which are excited by energy-transfer from the host emitter giving rise to various color emissions (blue, green, yellow and red), including *white*.[48] Due to their high fluorescent quantum efficiency, these dopants have been shown to enhance both the efficiency as well as stability in many cases. It is worth noting that the fluorescence intensity of these dyes decreases at high concentration by a phenomenon known as "self-quenching". Thus, they are not suitable for use as an emitter layer in their own right.

5.1 Electron Transport Emitters

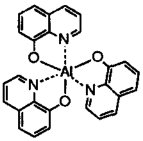
The *host* emitter can also be called the *primary* emitter, which is the organic matericals that are responsible for the generation of the initial *exciton* from recombination of carriers at, or near, the interface. From the materials point of view, the primary emitter can be further classified into the following three categories depending on their intrinsic carrier-transporting properties.

5.1.1 Metal Chelates

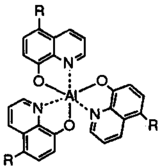
The most prevalent electron-transporting emitter layer used in organic EL devices is the aluminum 8-hydroxyquinoline chelate (AlQ_3) which emits in the green with a broad emission peaking at 530 nm. Its DMF solution photoluminescence quantum efficiciency is about 11%[49] and its thin film room temperature PL quantum efficiency is reported to be around 32% independent of film thickness from 100 Å to 1.35 μm.[50] Electron mobility of AlQ_3 was estimated to be around 10^{-5} $cm^2/V/s$ [51] with its hole mobility only about 1/100th as much.[52]

One of the best attributes of AlQ_3 is its propensity to form good thin film upon vacuum deposition, and it has a relatively high T_g (175 ^oC) as well. Vapor-deposited AlQ_3 films consist of a solid solution of two geometric isomers (called *meridianal and facial*) which may hinder the recrystallization of AlQ_3 films and explain their long-term stability in a glassy form. From a dye chemist's point of view, AlQ_3 can also be considered as a *metallized pigment*, which is invariably more stable than a "dye". In addition, it is also *organometallic* which may provide the best compromise for mediating phase separation between a metallic phase (Mg:Ag) and a pure organic phase (hole transport material). The molecular geometry of AlQ_3 determined by single-crystal X-ray crystallography is roughly shaped as a ball.[53] It is believed to have little, or no, propensity to form *exciplex* with an electron-rich hole-transporting molecule at the interface. Other metal *tris*(8-hydroxy-quinolinate)'s have been tried in EL heterojunction devices, e.g., Ga, In, and Sc. It was found that GaQ_3 has a thin film PL quantum efficiency of only 1/4th that of AlQ_3. However, its light emitting devices have an approximately 50% higher power efficiency than AlQ_3, suggesting that the GaQ_3 is a superior emitter material for display applications.[54]

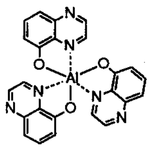
Many derivatives of AlQ_3 have been synthesized and studied as organic light emitting materials, among which, the C-5 substituted ones are the most prevalent (e.g., R = F, Cl, NO_2).[55] In an effort to lower the LUMO of AlQ_3, both aluminum *tris*(5-cyano-8-hydroxquinoline) (R = CN) and *tris*(5-hydroxyquinoxaline) have been synthesized.[56] However, there were no appreciable differences observed in the peak wavelengths or line widths in the absorption or PL spectra of AlQ_3 and Al(Q-CN)$_3$. This result is also consistent with the ZINDO semiempirical MO calculation.



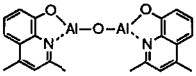
AlQ$_3$



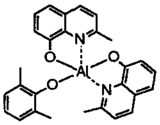
Al(Q-R)$_3$



Al(Q-N)$_3$



(QAl)$_2$O

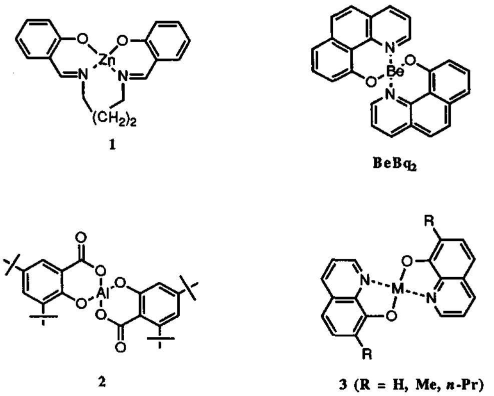


Q_2Al-OAr

Many efforts have been spent to shift the emission of AlQ_3 to the blue. The chelate (QAl)$_2$O, based on the 2-methylquinolin-8-ol derivative, was first exploited to obtain an EL blue emission.[57] However, its stability is far from satisfactory. A more stable blue emission was achieved by using the modified chelate Q_2Al-L where Q is 2-methylquinolin-8-ol and L is a phenolic or an aryl carboxylate derivative.[58] A representative example is shown as structure **Q_2Al-OAr**. A bulky substituent, such as 2,5-dimethylphenol which effectively shields the Al^{+3} from nucleophilic attack, was found to improve stability.

Other metal chelates that have been used as the emitter layer in EL devices are exemplified in **Figure 3**. The intramolecularly linked *bis*(salen)$_2$-metal chelates were patented by Sanyo.[59] Usually, *salen* as a ligand does not give rise to very stable chelates. However, the covalently bonded *bis*(salen)$_2$Zn (1) appeared to be exceptional. The doping of *bis*(salicylato)aluminum (2) was reported to enhance the performance of AlQ_3 in a dual-layered device.[60] Organic electroluminescent devices using metal complexes of 7-substituted-8-hydroxyquinoline 3 (M = Zn, Be, Mg) as the emitter have also been developed.[61] The emissions of these devices which have a luminance of more than 3000 cd/m^2 are green or yellow. In particular, the EL device with ZnQ_2 (3, R = H) has a luminance of 16,200 cd/m^2.

Fig. 3. Electron Transport Metal Chelates



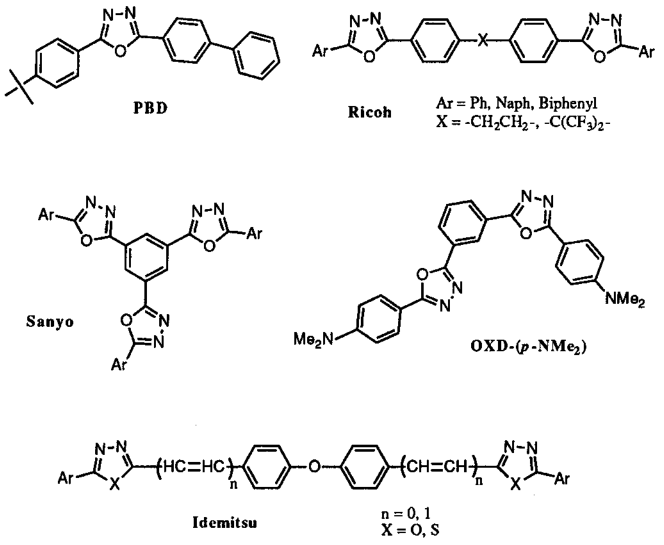
The most noteworthy host emitter by far, is the green fluorescent $BeBq_2$, *bis*(10-hydroxybenzo[*h*]quinolinato)beryllium, which has a peak emission of 516 nm and achieved a luminous efficiency of 3.5 lm/W in a standard cell configuration like DL-A.[62] A luminance of more than 10,000 cd/m^2 was recorded with a modified device structure of [ITO/MTDATA/TPD/$BeBq_2$/Mg:In] in which, by doping with *rubrene* in the TPD layer, the operational stability was greatly improved (Section 6.2).[63]

5.1.2 Oxadiazoles

*B*iphenyl-*p*-(*t*-butyl)phenyl-1,3,4-oxadiazole (**PBD**) was one of the first oxadiazoles used as electron transport material in the triple-layered device shown in **TL-C**.[64] Many variations of 1,3,4-oxadiazole (OXD) have since been found to be useful as primary emitters in a dual-layered EL format. **Figure 4** shows a list of representative examples with the associated companies (Ricoh[65], Sanyo[66], and Idemitsu[67]) who hold the patents.

Fluorescent dyes that exhibit *blue* emission draw a special interest since blue emission is hard to get in inorganic semiconductor devices.[68] A family of oxadiazole derivatives (OXD) were synthesized[69] with the aim of obtaining electron transporting blue emitting materials. In cells fabricated similar to **DL-A** using TPD as HTL, the EL device with OXD-(p-NMe_2) showed the highest luminance of 1,000 cd/m^2 at a peak emission of 480 nm and a current density of 100 mA/cm^2. These performance data seem to suggest that substitutions of the *p*-dimethylamino group in OXD tend to produce a much brighter luminance than, for example, the *t*-butyl group.

Fig. 4. 1,3,4-Oxadiazoles



PBD

Ricoh Ar = Ph, Naph, Biphenyl
X = $-CH_2CH_2-$, $-C(CF_3)_2-$

Sanyo

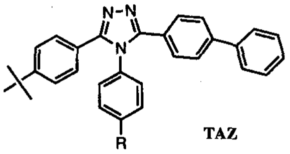
OXD-(*p*-NMe_2)

Idemitsu n = 0, 1
X = O, S

Carrier transport properties of oxadiazoles can be modified by changing the substituents. With strong electron donating groups such as amino groups, oxadiazoles can be changed to become hole transporting. From the materials point of view, the oligomeric forms of oxadiazoles generally improved the thin-film morphology when compared to the parent PBD. Idemitsu also patented the sulfur analog, 1,3,4-thiadiazole which did not appear to perform any better than the OXD's.

5.1.3 Triazoles

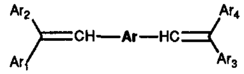
Replacing the oxygen in 1,3,4-oxadiazoles (OXD) with nitrogen, one obtains the derivatives of 1,2,4-triazole (TAZ) which emits in the blue (464 nm). TAZ has been shown to have a higher electron transporting capability than that of OXD.[70] In addition, TAZ's can be structurally modified more readily by introducing substituents on the *para* position of the phenyl ring to either control its morphology, or to alter its reduction potential. Due to the fact that it has a relatively high LUMO (exciton energy) level, it was used as what Kido called the "exciton confinement layer" in a triple-layered cell structure shown in TL-C. By controlling the thickness of this layer, one can mix the luminescent colors from two different emitting layers to achieve *white.*



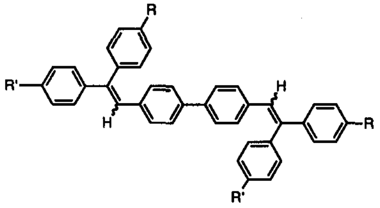
TAZ

5.1.4 Distyrylarylenes

One of the most significant developments in the area of blue emitting materials was announced by Idemitsu[71] who has patented a series of di(styryl)arylenes (DSA) which typically emit around 470-480 nm using TPD as the hole-transporting material and AlQ_3 as the electron-transporting material in a triple-layered device as shown in TL-C. EL brightness of 1,900-2,280 cd/m^2 at a driving voltage of 11-12.5 V which corresponds to a current density of 93-95 mA/cm^2 and a power efficiency of 0.5-0.6 lm/W was reported for DPVBi, DTVBi and DTBPVBi.[72] These type of materials will be discussed further in connection with the blue dopants later.



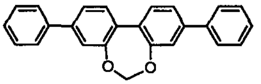
DSA

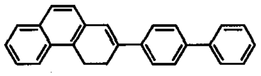


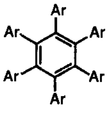
DPVBi (R = R' = H; Blue, λ_{max} 475 nm)
DTVBi (R = R' = Me; Blue, λ_{max} 475 nm)
DTBPVBi (R = R' = *t*-Bu; Blue, λ_{max} 475 nm)

5.1.5 Arylenes

One of the most ambitious and broadest patents on electron-transporting emitters used in organic EL were issued to Ricoh in 1991.[73] They have covered the general formula of $[B]_m$- $[A]_n$ where B = Benzene, Naphthalene, Anthracene, Pyridine, Quinoline, Phenanthrene; and A = Phenyl, Biphenyl, *p*-(cyano)phenyl, 3-Pyridyl, 2-Thienyl. Substitution of electron withdrawing groups or heterocyclic compounds is believed to enhance its electron-transporting property. Their data on EL performance was somewhat sketchy. Most of these compounds performed similarly to *terphenyl* or *quarterphenyl* derivatives; both of which emit in the blue. Representative compounds were shown as follows:



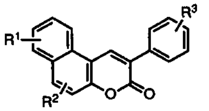


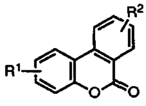


Ar = Ph, Biphenyl, *p*-(CN)Ph, 3-Pyr, 2-Thienyl

5.1.6 Coumarins

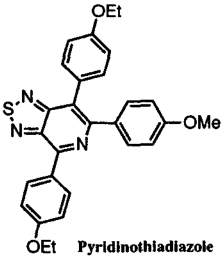
The structures of benzo-annulated coumarin derivatives which have been shown to work as electron-transporting emitters[74] are shown below.



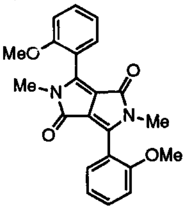


5.1.7 Other Heterocycles

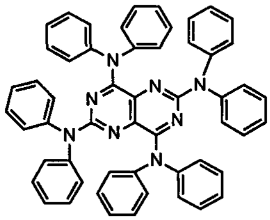
Mitsubishi patented the pyridinothiadiazole derivative as both a green emitter and a electron-transporting material[75] while the diketopyrrolopyrrole (DPP) derivatives were patented by Kudo.[76] The DPP emits in the yellow-green and yellow-red regions depending on substitutions. Kudo was able to show an OEL cell fabricated totally by a spin-coating method which resulted in no pin-hole by X-ray scattering analysis. Tetradiphenylaminopyrimido-pyrimidine (TDPP) and related fluorescent compounds were patented by Pioneer.[77]



Pyridinothiadiazole



DPP



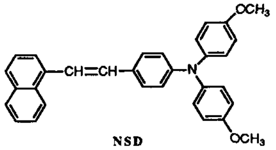
TDPP

5.2 Hole-Transport Emitters

Hole-transporting emitting materials are not as common as the electron-transporting materials mentioned above. In order to confine the exciton generated near the interface, one needs an electron-transporting layer inserted between the cathode and the hole-transporting emitting layer as shown in cell configuration DL-B or the triple-layered type TL-C.

5.2.1 Electron-Rich Styrenes

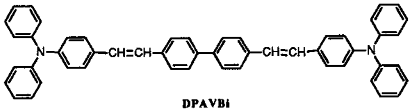
One of the earliest example of emission originated from the hole-transporting layer was the triarylamine derivative NSD shown below. This compound was reported by the Kyushu group who used PBD as the electron-transporting material in the triple-layered structure TL-C. A bright electroluminescence over 1,000 cd/m^2 in the blue was oberved from this device.



NSD

5.2.2 Bis(styryl)amines

One of the major advances in blue emitting materials used in EL devices recently was due to Idemitsu[78] who patented the general structure of D-R^{1}C=CR^2-[Ar]$_2$-R^{1}C=CR^2-D as a hole-transporting emitting layer (EML) where D = triarylamine, and R^1 and R^2 are various aryls, typically, Ph. One example, known as DPAVBi, which can be synthesized from the corresponding Wittig-Horner reaction[79] is shown below.



DPAVBi

Luminescence efficiency as high as 2.1 lm/W in the low-luminance region of 135 cd/m^2 using an [ITO/DPAVBi/PBD/Mg:Ag] device structure was observed in the blue-green region. The external quantum efficiency was estimated to be about 1.5% and the brightest luminance obtained was 4,000 cd/m^2.[80] Transient EL measurements have shown that holes were transported with large mobility on the order of 10^{-3} cm^2/V in the emitting layer and recombine with electrons to generate singlet excited states as the source of light emission.[81] The energy diagram for the device structure is shown in **Figure 5**. By substituting the electron-donating *p*-diarylamino group into distyryl arylenes (DSA), I_p of DSA (5.9 eV) decreases to 5.5 eV which lowers the energy barrier for hole injection by 0.4 eV. Therefore, the hole can be easily injected from ITO to the EML (DPAVBi) interface without needing an additional hole transport layer (HTL). Furthermore, the hole blocking role of the electron transporting PBD is also evident from the energy diagram. It effectively prevents the hole from moving to the cathode by the large energy barrier of 0.8 eV at the EML/PBD (ETL) interface, thus, allowing efficient recombination to take place.

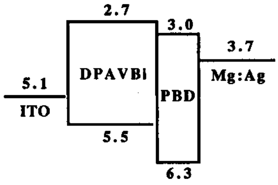
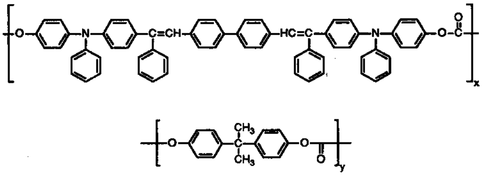


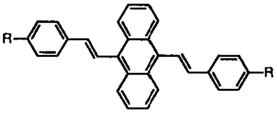
Fig. 5. Energy diagram of Idemitsu's multilayered EL device

The same company also patented a non-conjugated, co-blocked polymer (based on polycarbonate and a Ar_3N-stilbene type of emitter) which has a structure similar to that of DPAVBi.[82] With this hole transporting polycarbonate emitter (HT-PC), it was very easy to form a smooth and dense thin film at a thickness less than 100 nm without any recrystallization. For the EL cell with a **[ITO/HT-PC/PBD/Mg:Ag]** structure, a bright luminance of 130 cd/m^2 at a current of 80 mA/cm^2 with an applied voltage of 11 V was achieved.



It should be noted that the charge-carrier property of an emitter can often be altered depending on substitution. This is particularly true in the family of distyrylarylene (DSA) derivatives. Electron-donating substituents such as triaryl amines may make an electron-transporting emitter into hole-transporting.

Other examples of carrier transport properties of emitters, which are altered by electron-donating or electron-withdrawing substituents, were reported by the Kyushu group.[83] They used three 9,10-*bis*(styryl)-anthracene (BSA) derivatives to demonstrate that, while BSA-1 as emitter is electron transporting, both BSA-2 & 3 exhibit bimodal characteristics which allow the transport of both electrons and holes. Thus, it was demonstrated for the first time that a single layered device of [ITO/BSA-2 or BSA-3 (100 nm-thick)/Mg:Ag] showed similar luminance-current density profiles, which were comparable with the conventional two-layered devices as described in DL-A or B. On the contrary, while **BSA-1** has a definitive propensity for electron transport, it also showed considerably low efficiency in the single-layered device. These findings prove the importance of three criteria in the choice and design of dyes for use in organic EL devices which are: (1) balanced injection of electrons and holes; (2) control of the location of charge recombination zones; and (3) confinement of produced excitons.

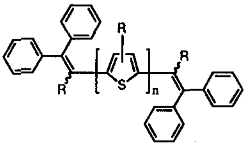


BSA-1 (R = CN) ***e-transport***

BSA-2 (R = NPh$_2$) ***bipolar***

BSA-3 (R = NEt$_2$) ***bipolar***

Oligothiophene derivatives of the following structure has also been used as hole-transporting emitters.[84] But, its EL efficiency is not as high as that of oxadiazoles (OXDs).



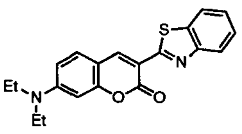
6. Dopant Emitters

As stated before, most organic fluorescent dyes tend to suffer from various degrees of "concentration quenching" which also causes the emission bands to broaden and *bathochromic* shift. This is particularly true in the solid state. Yet, in organic EL where emission in the three primary RGB colors is desired for display applications, organic dyes whose emission can be readily tuned by structure modification are best suited for such a purpose. This dilemma can be solved by doping or dispersing organic fluorescent dyes (guest) in a host matrix (emitter) whereby self-quenching can be minimized and emission from the guest molecule can be obtained by energy transfer. This principle applied to OEL was first demonstrated by the group in Kodak. In their patent,[48] it was claimed that almost all organic fluorescent dyes (as long as they are evaporable and energetically compatible) are useful as dopants. Some of the desired criteria for dopants to work in a full color EL display are: (1) high fluorescence quantum yield; (2) overlap between the emission of the host emitter and the absorption of the dopant to allow efficient energy-transfer; (3) emission λ_{max} at the blue, green, and red region of the visible spectrum; and (4) narrow emission bandwidth to maintain chromatic purity. A good dopant is also expected to increase the EL efficiency of the device in case the host emitter, such as AlQ_3, has a relatively low fluorescence quantum yield. In the following, we will review some of the most important developments in the use of dopant schemes that are promising in producing a full color EL display.

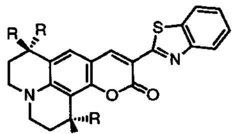
6.1 Green

AlQ_3 is the most studied green host emitter to date. As described before, it is electron-transporting so it is used together with a hole-transporting layer in a dual-layered cell shown in DL-A.

The laser dye, *Coumarin 6* was first used by Kodak as a dopant[17] that has peak emission at 500 nm (bluish green) and a near unity fluorescence quantum yield. It also showed a severe self-quenching problem at high concentration. However, when it was doped into the AlQ_3 layer (to the extent of about 1%), only EL originated from *Coumarin-6* was observed. This phenomenon is attributed to the efficient energy transfer from AlQ_3 to the dopant. What was remarkable about this device was that the EL efficiency of the doped cell was also increased to 2.5% compared with that of the undoped cell (1.3%). The dramatic enhancement of EL efficiency suggests that the highly fluorescent *Coumarin-6* is capable of intercepting some of the non-radiative decay pathways available to the excited AlQ_3. Other coumarin type of green dopants, such as the julolidyl-substituted *C-545* was patented by Pioneer[85] and the *tetramethyl*-julolidine dyes were claimed later by Toppan Printing[86] and TDK.[87] However, the earliest invention on the preparation of *tetramethyljulolidyl-coumarins* was patented by Kodak.[88]



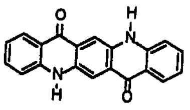
Coumarin-6



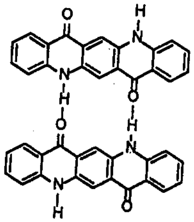
R = H, Me

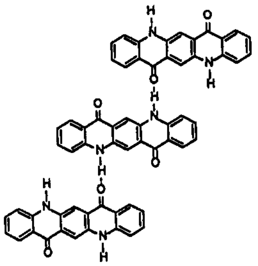
Another nice green dopant patented by Pioneer[89] belongs to the class of quinacridones (QA). When doped in AlQ_3 in a two-layered cell of DL-A, the parent QA exhibited a green emission of 540 nm. A record of 68,000 cd/m^2 at a current density of $1 A/cm^2$, which corresponds to an efficiency of 5 lm/W at the dopant concentration of 0.47%, was reported by the Pioneer group.[90] The EL efficiency of the doped cell was increased to about 3.7% which is better than that of the *Coumarin-6*.

The EL device using a quinacridone (QA) as the green dopant, however, is rather short-lived with a half-life of only about 500 hours. It is noted that the quinacridones have N-H functions that are capable of forming unstable hydrogen bonds with neighboring molecules possessing carbonyls. Such an inter-molecular aggregation would produce dimers or oligomers which may not be desirable for EL operation. Also,the secondary amines are usually not as stable in the high electric field as the tertiary amines. This rationale has led to the design and synthesis of a series of *N,N*-dimethyl substituted quinacridones as shown.

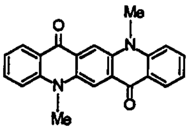


QA

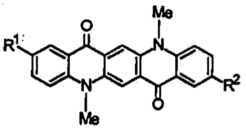




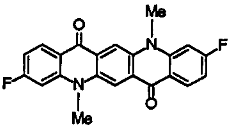
The remarkable improvement in EL stability has been achieved by using these substituted quinacridones as emitters.[91] For example, while the initial luminance output and the EL emission spectra of DMQA and QA are practically identical, the EL device with DMQA has a half-life of about 7000 hours compared to 500 h for QA.[92]



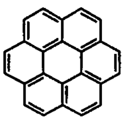
DMQA



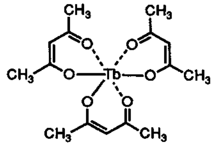
($R^1 = R^2 = F$, or CF_3)



Green emitters such as NSD, oxadiazoles, and distyrylpyrazine[93], which do not have a self-quenching problem, were often coated as a separate layer between hole- and electron-transporting layers in a triple-layered device such as TL-C. Extremely sharp green emission bands with a typical half-bandwidth of only 10 nm was obtained by $Tb(acac)_3$.[94] Recently, *tris*(2,4-pentanediono)-1,10-phenanthroline terbium (III) has also been disclosed.[95] These compounds were used as the emitting layer with TPD as the hole transporting and AlQ_3 as the electron transporting layers. The sharp EL emission peaking at λ_{max} 543 nm upon the application of a dc voltage is believed to arise from transitions within the 4f orbitals of terbium (III). In addition, the fluorescence of lanthanide complexes is based on an intramolecular energy transfer from the triplet state of the organic ligand to the 4f energy state of the ion. Therefore, the theoretical internal quantum efficiency, in principle, is not limited to 25%.

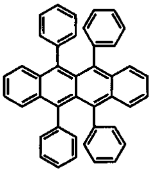


Coronene

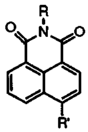


$Tb(acac)_3$

Other green dopants include naphthalimide (λ_{max} emission = 540 nm, green-yellow)[96] and coronene (λ_{em} = 500 nm).[97] The emission maximum of naphthalimide can be bathochromatically shifted to yellow by substituting a strong donating group at C-5 as shown.



Rubrene



Naphthalimide

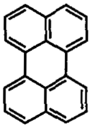
6.2 Yellow

One of the best yellow dopants for organic EL is *Rubrene* (λ_{em} = 562 nm). It can be dispersed either in the electron-transporting host emitter, *bis*(10-hydroxybenzo[*h*]-quinolinato)beryllium ($BeBq_2$) which has a PL emission peak at 515 nm or in the hole-transporting TPD layer which has a PL emission peak at 408 nm. The device structure of **[Mg:In/$BeBq_2$/TPD/MTDATA/ITO]** was reported by the group of

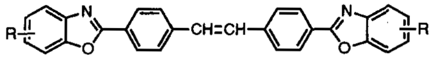
Sanyo. Both devices showed high luminance of more than 10,000 cd/m^2. However, the operational lifetime of *Rubrene* doped in TPD was shown to be *thirty-four times* longer (3554 h to reach half-decay when the initial luminance is 500 cd/m^2) as compared to only 110 h when the dopant was dispersed in the $BeBq_2$ layer. This result suggests that the operational stability of a device is highly dependent upon the emission site.

6.3 Blue

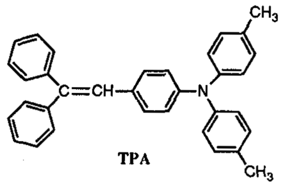
Anthracene was the first and the most studied blue material.[98] Its EL properties of thin films were investigated by the Kyushu group who found that its propensity to crystallize contributed to the formation of unstable amorphous thin films. Perylene was first used by Kodak as dopant for the blue emission.[57] Due to its energy mismatch with AlQ_3, it needs to be sensitized with a more *hypso-shifted* host emitter such as Q_2Al-OAr which was described in section 5.1.1.



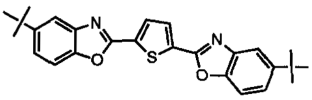
Perylene



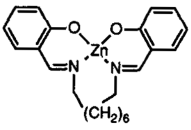
OB-1 (R = H)



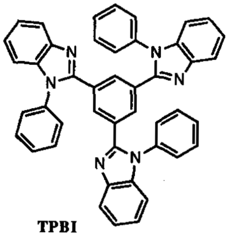
TPA



BBOT



AZM-Zn



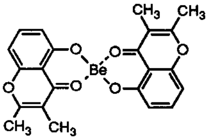
TPBI

Other examples of blue materials that have been used by Kodak as dopants include both EastoBrite OB-1 and BBOT as shown. The laser dye, BBOT has a perfect blue emission at 450 nm with very high quantum yield. However, its tendency to form exciplex or charge-transfer complex with hole-transporting materials, such as TPD, resulted only in green electroluminescence and a low EL efficiency.[99]

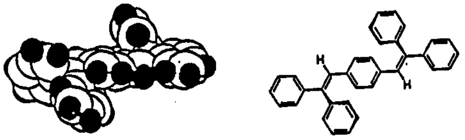
Certain azomethine-zinc complexes (AZM-Zn) were reported to be blue luminescent with a maximum luminance of 1,500 cd/m^2.[100] The stability of a *salen* ligated complex is, however, questionable. Strictly speaking, this type of material was not used as a dopant but instead was fabricated as a separate emitting layer to confine the exciton formation. The same can also be said about Saito's hole-transporting TPA and the electron-transporting oxadiazole (OXD) emitters which were described in the previous sections.

A series of N-arylbenzimidazoles, including the trimer, N-arylbenzimidazoles **TPBI**, was designed and synthesized recently for use as blue-emitting materials.[101] Besides blue emission, they are also capable of transporting electron efficiently. Multilayer organic EL devices with TPBI as the emitting layer produced highly efficient blue emissions and a lumininous efficiency of about 1.0 lm/W.

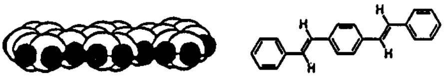
Beryllium and Sc (III) complexes of 5-hydroxy-4-chromone were used by the Sanyo group[41] as blue greenish dopants, in attempts to achieve a white light-emitting diode.



One should not leave this section without mentioning again the *distyrylarylene* (DSA) derivatives, $Ar_2C{=}CH{-}(Ar'){-}CH{=}CAr_2$, which was tauted by Idemitsu as one of the best blue materials to date for use in organic electroluminescence.[102] Surveying their patents, it appears that a luminance of over 1,000 cd/m^2 in the blue region of 440-490 nm was routinely observed in their EL devices depending upon the various substitution patterns of the structure. By molecular design and synthesis, the tri-substituted DSA compounds are **non-planar** due to the steric overcrowding of the *gem*-diaryl substitution at the terminal carbons.[103] The molecular conformation of DPVB is shown from the side elevation view as compared to the less crowded 1,2-disubstituted styryl derivative, DSB, in **Figure 6.** A bright blue emission of more than 6,000 cd/m^2 with an applied voltage of 13 V and a luminance efficiency about 0.7 lm/W for **DTVBi** as an emitting material was achieved. The peak intensity of the EL spectrum as well as that of PL spectrum was at about 475 nm with a half-bandwidth of only about 80 nm. The color was pure blue according to CIE chromaticity coordinates. The fact that the PL and EL spectra are identical suggest that EL can be attributed to an emission from a singlet excited state of molecules in the emitting layer. A tail in the longer wavelength region which is often attributed to the exciplex or charge-transfer complex (ECT) formation was not observed. It is concluded that these newly designed DSA compounds successfully avoid the ECT formation by virtue of their nonplanar molecular structure which prevents the molecules in EML from packing closely with the molecules in HTL at the interface.



DPVB

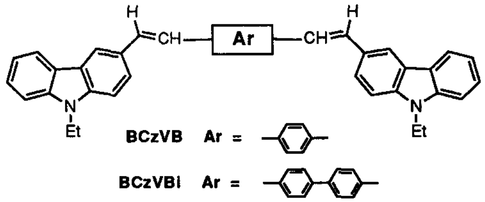


DSB

Fig. 6. Molecular conformations as generated by computer

In a paper published by the Idemitsu group,[104] it was disclosed that the tertiary amino-substituted dopants, BCzVB and BCzVBi,[105] have achieved what is believed to be one of the highest efficiencies in blue emitting OEL devices. Using a device shown in **Figure** 7 with respective energy levels outlined, they reported to have achieved a luminance efficiency of 1.5 lm/W and the external quantum efficiency was estimated to be about 2.4%. The device was fabricated by sequential evaporation of CuPc (copper phthalocyanine),[106] TPD, DPVBi, AlQ_3 as a hole injection layer (20 nm), HTL (60 nm), EML (40 nm), and ETL (20 nm), respectively. In spite of large energy mismatching (0.8-0.9 eV) between the EML and electrodes, stable carrier injection into blue emitting EML was achieved under a low voltage of 6-10 V. In a subsequent report from the same group, the luminous efficiency of this organic EL cell was said to have improved up to about 2 lm/W in the color range of blue with introduction of a "new dopant" into EML.[107] They also reported to have observed no enhancement by doping *perylene* into a DPVBi emitter (up to a concentration of 2 mol %), even though the emission was attributed to the radiation decay of the singlet excitation of perylene. Therefore, it appears that doping of the amino-substituted DSA molecules into the EML is a new effective way of enhancing the efficiency of blue emitting devices.

Finally, it was disclosed in their latest *SID 97* paper[108] that they were able to achieve a high EL efficiency of 6 lm/W and a half-life of more than 10,000 h for a device fabricated with a selected distyrylarylene (DSA) emitting layer containing an "amino-substituted DSA" dopant, driven under a constant current at an initial luminance of 100 cd/m^2. No other details, however, were available during the preparation of this manuscript.



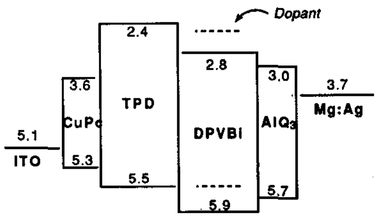


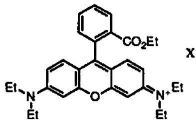
Fig. 7. Energy diagram of a blue multilayered EL device (---- denotes energy levels of dopants)

It is to be noted that BCzVBi by itself is a hole-transporting emitter. Transient electroluminescence was observed for the cell with the **[ITO/BCzVBi/Mg:Ag]** structure using short voltage pulse measurements. A response time of 20 ns, which is believed to be the fastest in organic EL, was recorded.

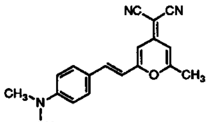
With the advent of the efficient DPVBi blue emitter in organic EL devices, a new RGB multi-color display system based on the principle of "color changing medium (CCM)" was reported recently by Idemitsu Kosan Co.[109] CCM is made up of organic fluorescent mediums which is capable of changing emissive color from blue to green or red. The efficiencies of RGB emission in this system are found to be higher than that of the *white* display with color filters. The fabrication process of CCM color system is also simpler than the process of making up of three individual RGB emitting layers. It is found that the conversion efficiencies of luminance from blue light to green or red light are 120% or 30%, respectively. A prototype of a 16x16 pixels RGB multi-color organic EL display in the size of 72 x 72 mm^2 has been fabricated with luminance and color coordinates in CIE chromaticity of B = 65 cd/m^2 (x = 0.12; y = 0.18), G = 150 cd/m^2 (x = 0.23; y = 0.65), and R = 40 cd/m^2 (x = 0.63; y = 0.32). The device could be operated under the pulse with a small duty ratio of 0.002 and the response time was only 600 ns driven at 13 V.[106] A new micro-patterning method of the CCM using a photolithographic process was also disclosed in this proceeding.

6.4 Red

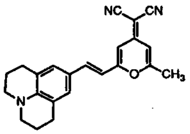
Red dopants having high fluorescent quantum yield are not as common as blue or green dopants. For the fabrication of "molecular" EL devices where dyes need to be vacuum deposited as thin films, it is necessary that the red dopants chosen possess a certain amount of vapor pressure and thermal stability under vacuum. For this reason, many well-known, ionic red laser dyes, such as rhodamine, sulforhodamine, and oxazine salts are not suitable for use as dopants in EL cells. However, by changing the counter-ion, rhodamine metal complexes dopants (X = $GaCl_4^-$, $InCl_4^-$, $TaCl_4^-$) were successfully used to produce orange emission.[110] Kodak chose the well-known laser dye DCM to work as a dopant in the host emitter AlQ_3.[17] DCM has a photoluminescent quantum yield in solution of about 78%.[111] Its emission maximum is at about 596 nm with a half-bandwidth of about 100 nm. The color of PL emission and quantum yield of DCM are both highly concentration dependent. At the optimum doping concentration of about 0.5%, the EL efficiency was about 2.3% which is more than 2x that of the undoped cell. However, the color measured on the CIE coordinates is only x = 0.56; y = 0.44, which therefore, appears orange. To shift the emission further to the red, the team at Kodak studied the julolidyl-substituted dye (DCJ) which has EL emissions peaking at about 610-690 nm. Once again, the emission is dependent on the doping concentration (the higher the concentration the longer the emission wavelength). It was found that at the optimum doping concentration of 0.57% where the emission intensity of DCJ was maximized, the AlQ3 emission could not be completely quenched. As a result, the combined emission still appeared somewhat "orangish" (red + some green).



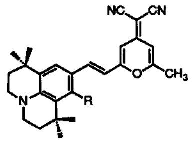
Rhodamine Metal Complex



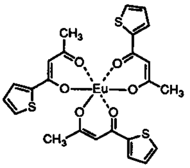
DCM



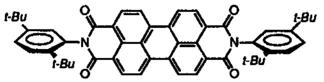
DCJ



DCJT



Eu(TTFA)3



TBPD

A desirable red region (CIE: x = 0.64; y = 0.36) could only be reached at a much higher concentration of doping (about 2%) but at the considerable expense of the overall EL efficiency. This concentration effect of emission maximum as well as EL efficiency was attributed to the increasing propensity of [Dye-Dye] interaction at the higher concentration.

This problem was later alleviated by inserting the bulky *tetra*methyl substituents at the C-1 and C-4 positions of *julolidine* (shown as DCJT) as "steric spacers" to minimize the potential interaction among dyes at high concentration.[112] The effect of the steric group in DCJT in offsetting the concentration quenching effect was manifested in its EL, which began to drop only when the DCJT concentration was greater than 1%. Its efficiency was maintained at a level similar to the undoped AlQ_3 cell at a concentration as high as 4%. In contrast, the EL efficiency of the DCJ doped cell decreased significantly at 1% concentration, and is only about half that of the undoped cell at 3 to 4% concentration. A similar *steric* effect is also responsible for preventing the *tetra*(t-butyl)-substituted perylenedicarboximide (TBPD) from self-quenching in the solid state.

From the point of view of a color chemist, the emission band of DCJT, when used as a red dopant in a full-color EL display, still suffers from its broad bandwidth band shape. At an optimum doping concentration, part of the emission band invariably falls into the near IR domain (beyond 700 nm) where human eyes are least sensitive. As a result, part of the radiant energy is lost and this is reflected in the drop in EL efficiency.[113] One way to narrow the emission band of organic dyes is by *rigidization* which also would shorten its Stoke shift. One candidate is magnesium phthalocyanine (MgPc) which was successfully used as a dopant by the Kodak group recently.[114] Unfortunately, MgPc emits too far to the red (692 nm) to be considered as a good dopant for visible EL. Recently, tetraphenyl porphine (TPP) has been used as a red dopant in a stacked pixel architectured EL color display.[115]

Another approach to the red emitter problem is by using Eu(III) complexes, which have a very sharp emission band at approximately 620 nm. Unfortunately, most Eu(III) complexes are not stable enough to be evaporated. As such, they are not suitable as red dopants for "molecular" organic EL devices. Nevertheless, Kido[116] has utilized tris(thienoyl-trifluoroacetonato)Eu complex, $Eu(TTFA)_3$ which was molecularly dispersed in PMPS as a red emitter layer in a EL device structure of **[ITO/doped PMPS/PBD/Mg:Ag]**. By adding an extra ligand of 1,10-phenanthroline to stabilize $Eu(TTFA)_3$,[94] the resulting europium complex **[$Eu(TTFA)_3Phen$]** can indeed be vacuum-deposited to form thin film under UHV conditions at a base pressure of about 10^{-9} hPa.[117]

6.5 White

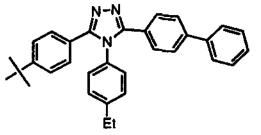
Organic EL white-light emitting devices are gaining increasing attention in the marketplace because they can be used as paper-thin light sources or they can also be used as a backlight in LCD as well as full-color displays. Nevertheless, there are few organic white-light emissive devices known.

One of the ways to achieve color mixing in a double-layered device such as DL-A or B was by way of incomplete energy transfer with partial doping which was first reported by the Kodak group.[118] They demonstrated that, in a device with an electron-transporting green-emitting AlQ_3 which was partially doped with a red-emitting DCJ dye, the resulting light becomes a mixture of the lights from both of the two emitting materials, thus producing a *yellow* light. It is, therefore, conceivable that by replacing the green host emitter with a *blue* one, a white-light should be readily generated by the same technique. For example, Sato disclosed an organic electroluminescent device, capable of emitting white light which was made by stacking a blue light emitting layer next to the hole transporting layer followed by a green light emitting layer having a region containing a red fluorescent dye.[119]

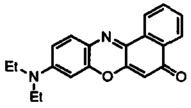
Following the leads from a polymeric white-light emitting device[120] in which it was doped with three kinds of fluorescence dyes, each emitting blue, green, or red, Kido was first to demonstrate that white-light can be obtained by mixing blue, green, and red emissions from three separate emitting layers as depicted in cell structure TL-D. They used a hole-transporting TPD as a blue emitter (λ_{em} 420 nm) and a hole-blocking 1,2,4-triazole derivative (*p*-EtTAZ) which has an emission at around 380 nm as an exciton confinement layer that transports electrons, but effectively blocks holes. An electron-transporting AlQ_3 was used as green host emitter (λ_{em} 530 nm) and Nile Red which has an emission peak at 600 nm was used as the red dopant. The thickness of *p*-EtTAZ was important. A typical working white light-emitting device was fabricated as: **[ITO/TPD** (400 Å)/***p*-EtTAZ** (30 Å)/**AlQ_3** (50 Å)/**Nile Red** (1 mol % doped) **AlQ_3** (50 Å)/AlQ_3 (400 Å)/**Mg:Ag]**. As can be see, the fabrication process was quite elaborate. Notwithstanding, a bright white light, over 2000 cd/m^2 was successfully obtained at a driving voltage of 16 V. However, the lifetime of this device was not reported.

Kodak recently described a white EL device comprising only one lumiescent layer in which a red fluorescent dye, BODiPi, is uniformly dispersed in a blue emitting host, such as **Q_2Al-OAr**. By selecting an appropriate guest concentration in the host, a combination of these two emissions is produced, resulting in white electroluminescence.[121] Recently, in the *SID 97 Conference*, an interesting lanthanide complex, *tris*(4,4,4-trifluoro-1-phenyl-1,3-butanediono)-1,10-phenanthroline dysprosium (III), was shown to be potentially applicable as a white-light emitting material in a single-layer EL device.[94] $Dy(BTFA)_3Phen$ complex is sublimable and its thin film luminescence color in terms of CIE chromaticity is [x = 0.36; y = 0.38].

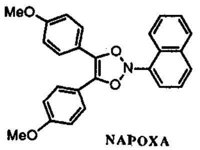
Other methods can also be used to produce white EL. For instance, using a tuned microcavity[122], the AT&T group[123] reported a white organic LED using a broad band emitter such as AlQ_3. The microcavity and the optical mode of the EL emitter can be tuned to select or de-select certain bandwidths of photons that can be directed outside the cavity.



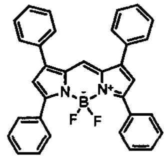
p-EtTAZ



Nile Red



NAPOXA



BODIPI

The same group later published the fabrication and characterization of a white-light emitting OEL device, which has a thin layer of a blue-emitting NAPOXA [2-naphthyl-4,5-bis(4-methoxyphenyl)-1,3-oxazole] sandwiched between TPD and AlQ_3. This architecture, which places the higher energy emitting material NAPOXA next to the hole transporter, permits efficient exciton recombination in, and light emission from, both NAPOXA and AlQ_3.[124] NAPOXA has a broad luminescence spectrum which spans the range 400-650 nm with a significant fraction of emission occurring at blue wavelengths where AlQ_3 emits poorly.[125] The proportion of red to green wavelengths in the electroluminescent spectra was tailored by incorporating low percentages of the reddish dye DCM into a thin layer of AlQ_3 located 300 Å from the NAPOXA/AlQ_3 interface. With this combination, they achieved white (CIE: x = 0.31, y = 0.41) light emission with a brightness reaching 4,700 cd/m^2 and an efficiency of 0.5 lm/W. These attributes should prove useful for low power backlights for small area and low information content display applications.

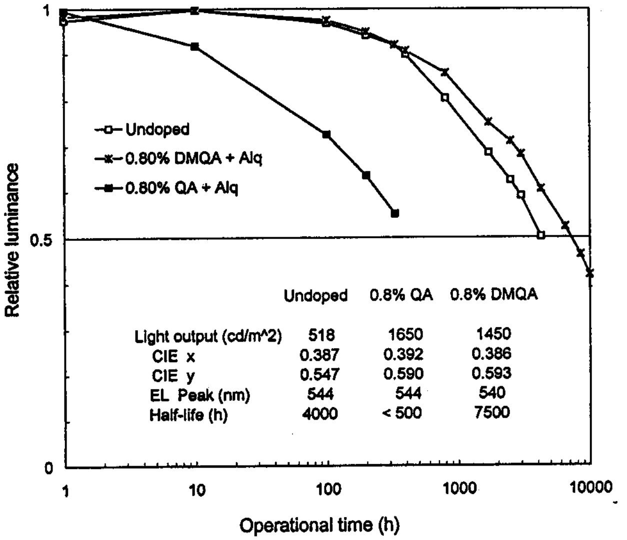
7. Stability

Practical applications using organic EL devices are only feasible if the devices are sufficiently long-lived under normal operating conditions. Here lies the most difficult challenge in the development of organic EL technology. The problem is a complicated one. In general, non-radiative decay mechanisms are poorly characterized in most organic luminescent solids, particularly in the ultrathin films used in most EL structures. In addition, the degradation pathways due to the EL process are necessarily dependent on the specific device structure, electrodes, and the operating ambient.

However, most organic EL devices reported so far have a rather short operational lifetime (with some reports which did not even mention stability at all), ranging from a few hours to several hundred hours. This instability has been attributed to the deterioration of the organic[126] as well as the electrode layers[127] and is highly dependent on the device configuration.[128] Indeed, by using a new EL configuration with a doped hole-transport layer as the emitter, significantly improved stability (half-life about 3,600 h) has been obtained.[62]

For "undoped" cells, highly stable organic electroluminescence devices based on vapor-deposited AlQ_3 thin films have been reported recently.[129] The improvement in stability is derived from several factors including: (1) a multilayer thin-film structure with a CuPc stabilized hole-injection contact; (2) a NPB hole-transport layer; and (3) an ac drive wave form. These emissive devices have shown an operational half-life of about 4,000 h from an initial luminance of 510 cd/m^2.

This stability can be improved further with the judicious selection of dopants in the host AlQ_3 emitting layer. Fig. 8 compares the stability of three green AlQ_3 devices driven by a constant current of 20 mA/cm^2, using an undoped and two doped emitters. For the quinacridone (QA)-doped AlQ_3, the initial luminance (1,600 cd/m^2) is almost tripled that of the undoped device because of the enhanced luminance efficiency. The stability is, however, rather poor, providing a $T_{1/2}$ of only about 300-400 h. With *N,N*-dimethylquinacridone (DMQA) as dopant, an EL device with superior stability and high luminance has been achieved. The $T_{1/2}$ is more than 7,000 h with an initial luminance of 1,400 cd/m^2.



	Undoped	0.8% QA	0.8% DMQA
Light output (cd/m^2)	518	1650	1450
CIE x	0.387	0.392	0.386
CIE y	0.547	0.590	0.593
EL Peak (nm)	544	544	540
Half-life (h)	4000	< 500	7500

Fig. 8. Stability of ALQ3 EL device at 20 mA/cm^2

These examples show that the EL stability can be profoundly affected by the particular choice of dopant, among other factors. The $T_{1/2}$ value is dependent on the luminance level produced by the EL device, and a longer $T_{1/2}$ is obtainable for operation at a lower luminance. Thus, a half-life in execess of 50,000 hours can be reasonably projected for the DMQA-doped AlQ_3 device operating at an initial luminance of about 100 cd/m^2.[130]

With these lifetimes, applications ranging from directly modulated fast-switching light sources for optical imaging to large-area full-color flat panel displays can be envisioned. Whereas much more work remains to be done, particularly in further improving the EL stability, we are confident that organic electroluminescence will prove to be an important technology with a "bright" future.

8. Other Applications

The advent of thin-film organic electroluminescent technology has inspired many researchers working in the field of opto-electronics to find other novel applications. A new type of light transducer consisting of an organic EL diode on a photoconductive amorphous silicon carbide (a-SiC:H) film has been successfully designed, which performs efficient light up-conversion from red to green with quantum conversion of 1% with the assistance of a newly observed photocurrent multiplication in a-SiC:H film.[131] It is predicted that, by using a photoconductive semiconductor having a much smaller bandgap, IR-visible light conversion may be possible, thus, leading to new types of display devices such as an IR-visible image convertor and an EL display addressing by IR diode laser. It is further speculated that this new light transducer technology may one day be used as an opto-electronic device for two-dimensional optical computing.

Another application, reported by the same group, is related to the narrow beamed light emission from a new type of organic EL diode. Its organic layer was sandwiched between two metal layers acting both as charge injecting electrodes and mirrors. EL from the organic film edge showed a much sharper spectrum and about a 100 times larger emission density compared with that from the film surface of conventional EL diodes. EL output can also be tuned from blue to green by varying the organic layer thickness.[132] It is conceivable that this device may lead to the realization of a thin-film organic diode laser.

9. Outlooks

Much progress has been made in organic electroluminescence in recent years. Largely, it is due to the continuing discovery of new and improved EL materials. From small fluorescent molecules to conjugated polymers, intense research in both industrial and academic laboratories has yielded organic EL devices with remarkable efficiencies and operational stability. As this review has shown, prototypical materials such as AlQ_3 and DSA have achieved luminous efficiency well in excess of *several* lm/W, and EL operation at 100 cd/m^2, with half-life greater than 10,000 hours has been demonstrated.

Further improvement in the organic EL device performance can be anticipated as more materials are being designed and synthesized by organic chemists specifically for EL applications. The molecular design criteria for high fluorescence efficiency and glass transition temperatures are well understood. The classic rules of rigid and sterically hindered molecular structures are generally applicable to the design of organic EL materials. Less clear, however, is the dependence of the carrier transport characteristics on the molecular structure. As the carrier transport is related to the magnitude of the injection current through the EL device (the light output), it is important to be able to design EL materials with superior hole or electron mobilities. This task is challenging, considering that there are additional constraints that other EL material parameters, such as fluorescence efficiency, cannot be degraded significantly in the process.

Although organic EL devices have achieved long operational stability, the material issues underlying the EL degradation are still poorly understood. Probable causes for degradation such as interfacial interactions between layers, electrochemical and excited-state reactions, and thin-film phase changes have been suggested. However, none have been conclusively proven to be the key degradation mechanism. More analytical effort would be needed in sorting out the degradation pathways. Particularly important is the identification of chemical species responsible for the device instability, as such analysis could provide insight into the design of new and improved EL materials.

Commercial interest in organic EL technology has been the main driving force in fueling the recent research and development activities. Anticipated applications are mainly in flat panel displays, including backlights for LCD, alphanumeric displays and dot-matrix panels for both low and high information content. Already, high-resolution monochrome green dot-matrix displays with 256 x 64 pixels by Pioneer Electronic Corp.,[133] RGB [75 x (7 x 3)] multi-color prototype EL display by Idemitsu Kosan Co. have been demonstrated[134,135] and advanced active matrix display development has been announced by TDK Corp. In comparison with other more mature display technologies such as LCD, organic EL is still in its adolescent stage. However, its promise of low-power consumption and excellent emissive quality with a wide viewing angle is unique among display technologies. These advantages will no doubt be successfully exploited and commercial use for organic EL devices will be realized in the near future.

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