Evaluation of Solid-State Light-Emitting Devices Based on the Tris-Chelated Ruthenium (II) Complex

by

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ABSTRACT

Organic light-emitting devices have the potential to create a new range of applications. They are versatile because their physical properties (color, emission efficiency) can be fine-tuned by the manipulation of their chemical structures. In this work, the novel technology of $Ru(bpy)_3^{2+}$-based devices was evaluated in the feasibility of commercialization. An overview was presented on current development and competing technologies within research and industry with regard to advantages and drawbacks of the technology of various organic light-emitting devices. The basic principles concerning the light emission from various devices were also presented. An intellectual property search on the technologies of the organic light-emitting devices revealed there was no patent to block the technology of organic light-emitting device based on $Ru(bpy)_3^{2+}$ complex. A brief economic analysis of $Ru(bpy)_3^{2+}$-based device was proposed for targeting the display markets.

Thesis Supervisor: Michael F. Rubner
Title: Professor of Polymer Materials Science and Engineering

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1.0 Introduction

The generic acronym OLED refers to organic light-emitting diode, compared to the (inorganic) LEDs that we are all familiar with. OLEDs come in two general forms. Both types of OLEDs have organic molecules as their active elements. Those that have relatively small organic molecules in their structures are typically refereed as small molecule OLEDs (SMOLEDs), and OLEDs that have relatively large molecules are called polymeric LEDs (PLEDs). SMOLED is a device that sandwiches carbon-based films between a metallic cathode and a transparent anode. The organic films consist of a hole injection layer, a hole transport layer, an emissive layer and an electron transport layer. When voltage is applied to the SMOLED cell, the injected positive and negative charges recombine in the emissive layer and create electroluminescent light. For PLEDs, the devices are created by sandwiching an undoped conjugated polymer between two proper electrodes.

A different type of light-emitting device is a light-emitting electrochemical cell (LEC). Polymer LEC can be made from a conjugated polymer such as poly (phenylene vinylene) (PPV) blended with a solid electrolyte that provides mobile ions. In such a device, the charge injection is more balanced and becomes fairly insensitive to the work function of electrodes due to the electrochemical nature of the operation. With such systems, the light-emitting devices with high efficiency and single layer were demonstrated. Recently, it has been showed that the $Ru(bpy)_3^{2+}$ complex can be employed in solid-state organic light-emitting devices. The salt-like nature of this molecule makes light-emitting devices based on $Ru(bpy)_3^{2+}$ complex operate in a similar manner to light-emitting electrochemical cells. In general, single-phase systems such as devices employing $Ru(bpy)_3^{2+}$ complex have the potential to show faster response time compared to polymer LECs since the light emission and ion conduction occur within the same phase.

Organic light-emitting devices are versatile because their physical properties (color, emission efficiency) can be fine-tuned by the manipulation of their chemical structures. They represent an alternative to the well-established display technologies

based on cathode-ray tubes and liquid-crystal displays (LCDs), particularly with respect to large-area displays for which the existing methods are not suited.

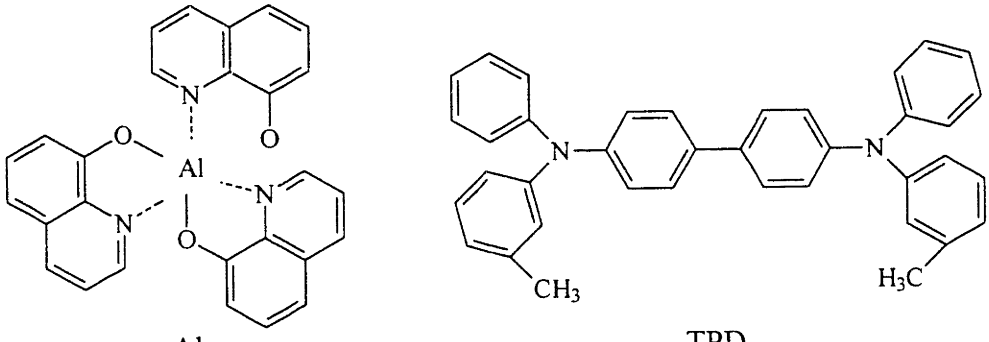
The purpose of this work was to evaluate if the $Ru(bpy)_3^{2+}$-based device is appropriate for an implementation into commercialization. The technologies of organic light-emitting devices are rather novel and the information in the literature study had to be retrieved from research papers. A number of papers were studied and relevant information was obtained. The literature study collected information about the advantages and drawbacks of the technologies of various organic light-emitting devices. The basic principles concerning the light emission from various devices were also presented. An intellectual property search was done to assess the directions that the technologies of the organic light-emitting devices are developing and the fundamental constraints of patents. Finally, a rough economic analysis of $Ru(bpy)_3^{2+}$-based device was evolved to estimate the investment of developing this technology to the commercialization stage.

2.0 Organic light-emitting diode (OLED)

2.1 Small molecule organic light-emitting diode (SMOLED)

Organic molecules were found to exhibit electroluminescence back in 1960.[1,2] Organic electroluminescence is obtained by simply placing a charge transporting and electroluminescent layer between two electrodes, one of which is transparent, and applying a suitable voltage. Charges of opposite polarity are injected at opposing electrodes and drift towards each other. At the point where they meet, they recombine to produce light. In the case where the organic molecules have low molecular weight, the devices are referred to as small molecule organic light-emitting diodes (SMOLEDs).

In practice, results obtained by using a simple single-layer device (small molecule organic light-emitting material between two electrodes) are rather poor. Practical application traces its origin to Tang *et al.* at Kodak, who introduced a double layer concept in 1987.[3] The devices were made by subliming N,N'-di-phenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) as hole transport layer, followed by aluminum tris(8-hydroxyquinoline) (Alq_3) for electron transport layer and electroluminescent layer, and a magnesium-silver alloy cathode.



Alq_3 TPD

Figure 1 Structural formulas for Alq_3 and TPD.

The typical SMOLED (Figure 2) consists of, in sequence, an indium tin oxide

(ITO) covered glass as the anode, multiple layers of organic films, and an evaporated metal film as the cathode. Device structures in SMOLEDs typically involve 5 to 7 organic layers.

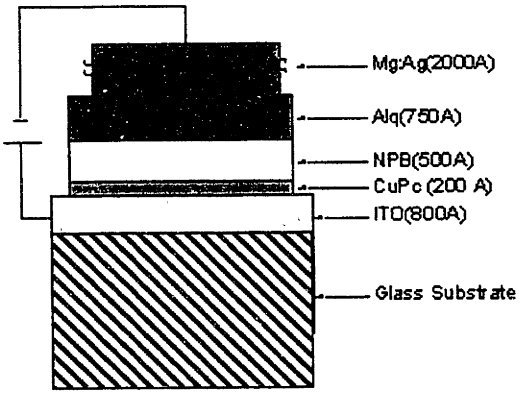


Figure 2 Cross-sectional diagram of the typical SMOLED. Reproduced from reference 4 with the permission from Prof. D. Jones, California Polytechnic State University at San Luis Obispo.

The operation of an OLED depends on the injection of holes from the anode and electrons from the cathode when a voltage is applied across the device. These carriers move through the organic layers until they meet each other and recombine to form excitons. Relaxation to the ground state is accompanied by the emission of light. One disadvantage of a single layer device is that, unless the energy levels of the cathode and anode are extremely well matched to those of the organic compound, the electron and hole currents are not balanced. Thus, the combination of electrons and holes occurs near the electrode. This causes quenching since the excitons can be deactivated by the adjacent electrode to lead to low efficiency in the conversion of electricity to light.[5)]

Considerably better balance can be achieved by using two organic layers which minimize the energy barrier between the electrode and the organic material.[6,7)] One is matched to the anode and transports holes and the other is

optimized for electron injection and transport. By choosing the material according to their properties of mobility and bandgap, the charged carriers could be injected and transported in an easier manner into the zone where an emission of light takes place. The difference in energy levels between the two organic layers creates a potential barrier at the interface. The barrier confines the holes and electrons and contributes to an increased recombination probability.

Another improvement is to introduce a third material specifically chosen for its luminescent efficiency. Now the three organic materials can be separately optimized for electron transport, for hole transport and for luminescence. Further optimization involves the introduction of additional hole and electron injection layers which lower contact barriers and form a staircase like path while blocking the opposite charge carrier from leaving the emission layer.[8,9,10] (Figure 3)

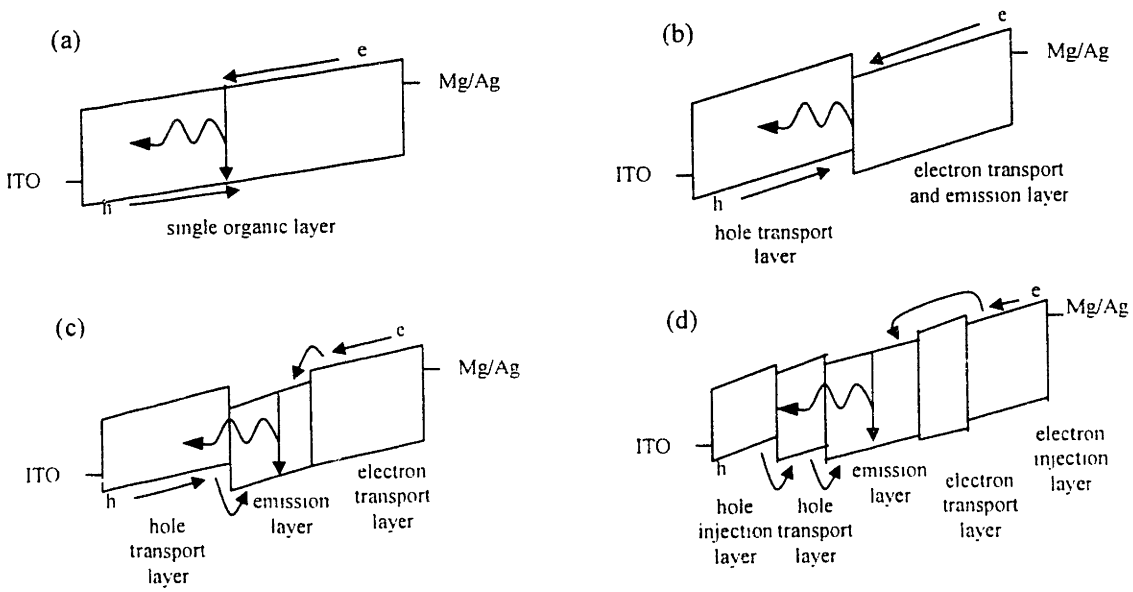


Figure 3 Schematic energy level diagram of (a) single organic layer (b) two organic layer (c) three organic layers (d) multi organic layers.

2.2 Polymeric light-emitting diode (PLED)

In 1990, J. Burroughes *et al.*, from the research group of Richard Friend at Cambridge University, found the first light-emitting diode made from a conjugated polymer.[11] The most widely used is poly(phenylene vinylene) (PPV) (Figure 4) with a bandgap about 2.3eV and thus emitting yellowish green

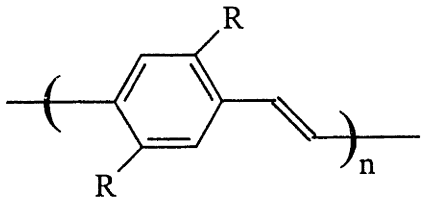


Figure 4 Structural formula for poly(phenylene vinylene) (PPV).

light.[12] PPV is made up of benzene rings (the phenylene unit) linked by a vinylene unit. The molecule is often adapted by adding alkyl side chains to the phenylene rings, thereby promoting certain desirable properties such as solubility.[13-17] The solution can then be processed easily, e.g. by spin coating or even ink-jet printing.

The simplest PLED (Figure 5) consists of a single layer of the conjugated polymer sandwiched between two well-known electrodes, a high work

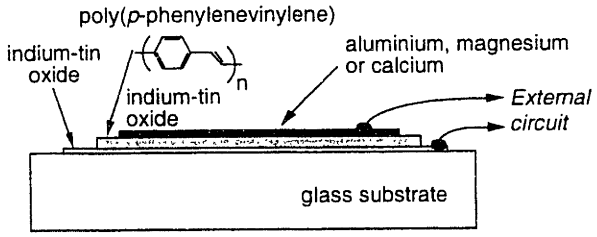


Figure 5 Scheme of a single-layer polymeric light-emitting diode (PLED).[18] Reproduced with permission from Nature Publishing Group (http://www.nature.com/).

function anode (ITO) and a low work-function cathode (Ca, Mg, Al, etc.).[18] In these devices, carriers of opposite sign are injected separately at opposing contacts when a sufficiently high voltage is applied. These carriers are mobile under the influence of the applied electric field. Formation of an electron-hole pair within the material may then result in the emission of a photon.

The energy level diagram for a single-layer PLED is shown in Figure 6. Under forward bias, electrons and holes are injected from the cathode and anode

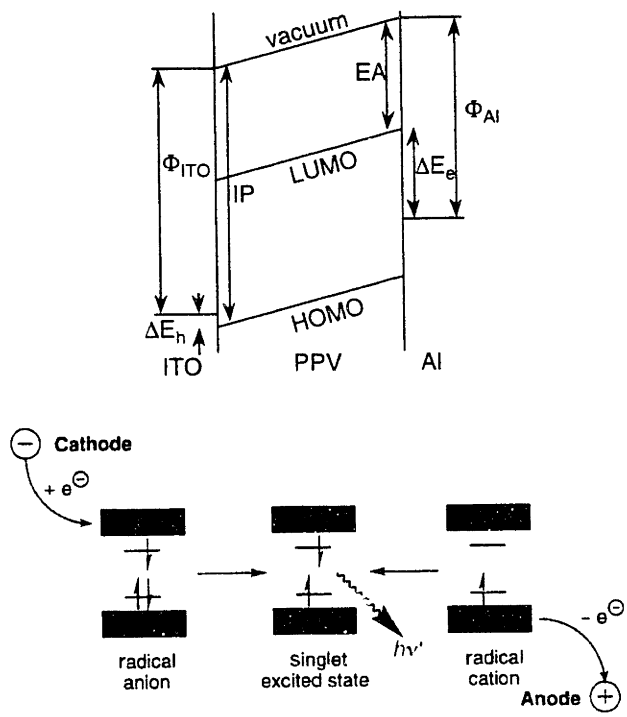


Figure 6 Schematic energy level diagram and for a single-layer PLED with structure ITO/polymer/metal cathode showing the ionization potential (IP) and the electron affinity (EA) of the polymer, the work function of the ITO anode and metal cathode(φ_{ITO} and φ_{Al}), the barriers to the injection of holes ((ΔE_e) and electrons (ΔE_h)).[12,18] Reproduced with permission from Wiley-VCH and Nature Publishing Group (http://www.nature.com/).

into the polymer respectively. The holes that are majority carriers and electrons that

are minority carriers can diffuse towards each other and finally recombine. From the view of photochemistry, electrons are injected into the lowest unoccupied molecular orbit (LUMO) to form radical anions and holes into the highest occupied molecular orbit (HOMO) to form radical cations. When a radical anion and radical cation combine, the singlet excited state is formed and then relaxes to the ground state by emitting light.

Since many conjugated polymers have ionization energies of about 5eV, high work-function materials such as gold, copper and indium-tin-oxide (ITO) are suitable for hole injection.[19,20] LUMO positions are typically located between 3eV and 1.5eV. Effective electron injection thus requires low work-function metals such as calcium.[12] However, these metals are very unstable in air and require device encapsulation. For a balanced charge injection, similar barriers (ΔE_e and ΔE_h) are needed.[21] In most polymeric systems, balanced charge injection is difficult to realize in single layer devices.

3.0 Organic light-emitting electrochemical cell (LEC)

3.1 LEC based on conjugated polymers

A light-emitting electrochemical cell, as first introduced by Pei *et al.*, is a light-emitting optoelectronic device consisting of a polymer blend embedded in between two electrodes, at least one of the two being transparent (typically indium tin oxide, ITO).[22] The polymer blend is comprised of a luminescent polymer, a salt and an ion conducting polymer in which the salt dissolves to form ions.[23-25] This composition determines the difference between LECs and polymeric light-emitting diodes (PLEDs). LECs are experiencing increasing scientific and industrial interest as solid-state sources of luminescence, thanks to their good electroluminescence efficiency, low driving voltages and ease of fabrication.[26,27]

Due to the presence of the mobile ions in the active layer, LECs facilitate charge injection at low applied voltages and make them fairly independent of the potential barrier height and of the trap densities at the interfaces of polymer and electrodes. The threshold voltage is practically given by the energy gap of the active polymer and therefore it is the lowest possible value for the chosen radiation.[28]

Figure 7 is a schematic diagram of LEC. The electrolyte is needed to provide ions, and the most used in LEC applications is poly(ethylene oxide), PEO, filled with lithium salt. By applying sufficient high voltage between the electrodes, cations and anions move in opposite directions (Figure 7a). The conjugated polymer is oxidized at the anode and reduced at the cathode. To maintain charge neutrality, the p-type and n-type doped layers formed during this initial step are stabilized by provision of counter ions that are available in the electrolyte (Figure 7b). Electrochemical doping occurs when the applied potential is larger than the energy gap of the polymer. The charge balance in this process is provided by cation and anion mobility into the blend. In the bulk a p-n junction is generated, and recombination processes take place with light emission (Figure 7c).

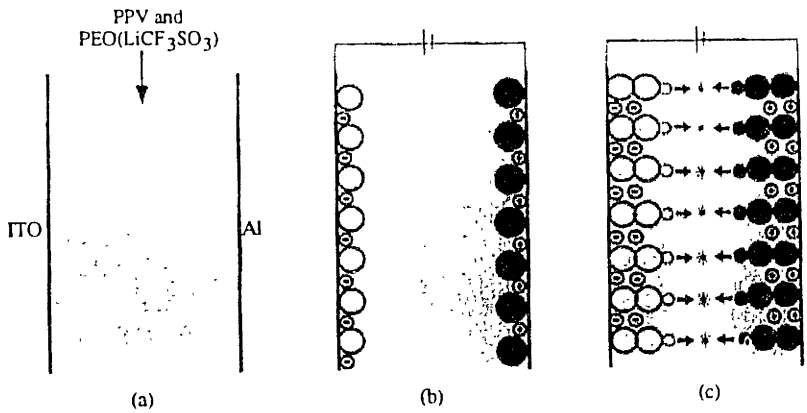


Figure 7 Schematic diagram of the electrochemical processes in a solid-state light-emitting electrochemical cell: (large open circle) an oxidized molecule, (large closed circle) a reduced molecule, (circled minus) an anion, (circled plus) a cation, (small open circle) a hole, (small closed circle) an electron, (asterisk) a photon.[23] Reproduced with permission from *J. Am. Chem. Soc.* **1996**, 118, 3922-3929. Copyright 1996 Am. Chem. Soc.

3.2 LEC from $Ru(bpy)_3^{2+}$-based complex

Electrogenerated chemiluminescence of tris-chelated ruthenium(II) complexes in solution has been studied extensively.[29-33] More recently, with the growing interest in solid-state OLEDs, efforts have been made to investigate ruthenium complexes in solid-state devices.[34-38] Most investigations have centered on *tris*(2,2'-bipyridine) ruthenium(II) complex [$Ru(bpy)_3^{2+}$](Figure 8) due to the exceptionally high stability of the corresponding reduced and oxidized species enabling annihilation efficiency close to 100%.[39]

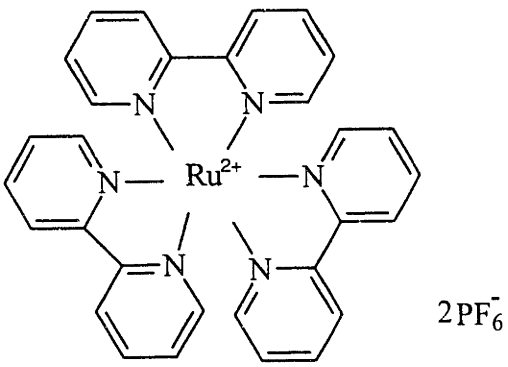


Figure 8 Chemical structure of tris(2,2'-bipyridine) ruthenium(II) [$Ru(bpy)_3^{2+}$] with PF_6^-counterions.

Rubner and coworkers reported that good light intensity can be achieved by a simple device based on "neat" thin films of $Ru(bpy)_3^{2+}$ /$(PF_6)_2^-$ using various ruthenium bipyridyl complexes.[33-36,40-44] These devices are similar to light-emitting electrochemical cell. [$Ru(bpy)_3^{2+}$] and related complexes carry a net 2+ charge and are compensated by negative counterions such as PF_6^- . The accumulation of these counterions near the anode (and the corresponding depletion near the cathode) enhances hole and electron injection, respectively. As a result, efficient devices can be made with air stable electrodes, in contrast to conventional organic light-emitting diodes that require low work-function cathodes. Therefore, it was shown that spin coated thin films of plain $Ru(bpy)_3^{2+}$ complex and its derivatives reach high efficiency and brightness at low operating voltage.[34,45]

Figure 9 shows a typical device with the $Ru(bpy)_3^{2+}$ complex sandwiched between two electrodes. Electrochemical process and concentration profile of the

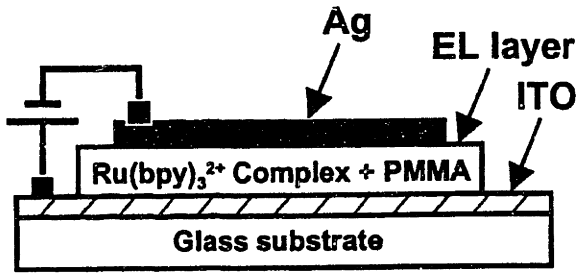


Figure 9 The device structure of a $Ru(bpy)_3^{2+}$-based device.[40] Reproduced with permission from *J. Am. Chem. Soc.* **2002**, 124, 4918-4921. Copyright 2002 Am. Chem. Soc.

$Ru(bpy)_3^{2+}$ complex are shown in Figure 10. Upon applying a voltage, there is the accumulation of the PF_6^- counterions near the anode and the corresponding depletion of PF_6^- near the cathode. The strong electric field due to the excess negative (positive) ionic charge near the anode (cathode) makes the ohmic contact for hole (electron) injection, regardless of the electrode work function.[46] Once a sufficient amount of counterions are moved, the oxidation and reduction of the Ru(II) complex occur. The regions composed of Ru(III)/Ru(II) near the anode and a region composed of Ru(II)/Ru(I) near the cathode are formed. At the junction of the two regions, the Ru(III) and Ru(I) recombine, and light emission occurs.

Unlike in liquid electrochemical cells where the oxidized and reduced states meet through diffusion of the whole complex,[47,48] in solid-state devices the charge transport occurs through charge hopping.[49] Charge hopping is the exchange of an electron or hole of two adjacent $Ru(bpy)_3^{2+}$ complexes with different oxidation states.[50]

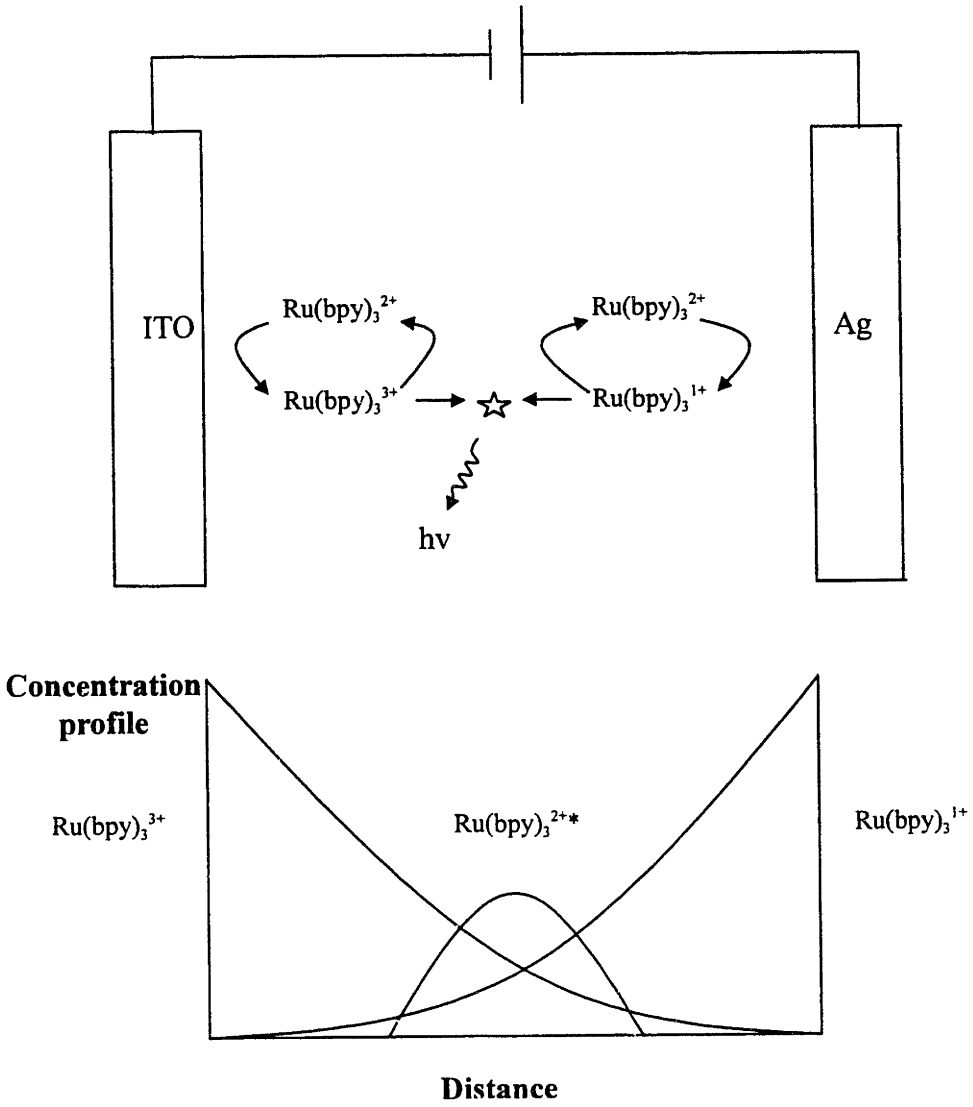


Figure 10 Schematic view of a light-emitting electrochemical cell using $Ru(bpy)_3^{2+}$ as the emitting species. The upper region shows the intermediates in the center of the thin film. The lower region shows expected concentration profiles of each species.

4.0 Analysis of advantages/disadvantages of OLEDs vs. LECs

4.1 Lifetime

Lifetime and reliability of OLEDs are major concerns in the practical application, although the fabrication technology has matured during the last decade. Lifetimes exceeding 10,000 hours have been shown.[51] Typically, luminance decreases with operation time and the higher brightness has the faster degradation. The lifetime corresponds to the time in hours before the overall luminance has been decreased below a given threshold value, often 50% of the initial luminance value.

In OLEDs with poor power efficiency, a high current density is needed in order to produce light. Only a few percentage of the power is applied to emit photons; the rest is converted to heat. The heat developed in the device causes degradation of the device. The increase of heat is proportional to the input current. The development of more power efficient devices would yield a reduction of the developed heat and a longer lifetime. The degradation process depends on colors that the material emits. To emit a blue color, a material with a larger bandgap is needed, which makes it harder to inject charge carriers and consequently more energy is needed. The high amount of current density makes the device more fragile and causes therefore a faster degradation for blue than for red and green emitting materials.

The lifetime of OLEDs depends strongly on such elements as efficiency, charge injection, mobility of carriers and so on. Charge carriers injected into organic layers are partially trapped and accumulate with time, eventually causing breakdown. This seems to be crucial for the OLED electrochemical long-term stability.

It is possible to reduce the degradation process by finding more power efficient organic materials. Doping the organic materials can result in a better power efficiency and a longer lifetime.[52] The triplet excited states are enabled to emit light instead of heat through phosphorescent doping. This not only yields a better power efficiency, but also reduces the time spent in the excited state. In the excited state the molecules could be considered more reactive and can cause a degradation of the emitting layer due to unwanted chemical reactions. The reduction of triplet excited states would also

lead to less heat generated and consequently to a better lifetime of the device.

Better multilayer structures can also bring a longer lifetime.[52] Depending on how the different layers are designed and in which order they are placed, the lifetime can be extended. The emitting layer plays a great role by affecting the lifetime. The addition of a hole transport layer enhances the lifetime by serving as a stabilizer for the flow of holes and by increasing an overall power efficiency due to more recombination. The both transport layers do not only function as transport medium but also in some case function as buffers prevent humidity and oxygen to diffuse into the active emitting layer.

Unlike OLEDs whose operation is like diodes. LECs can operate between forward and reverse bias. It is helpful to increase the stability by charge detrapping, which is similar to electronic devices; a reverse voltage pulse can be employed to allow charge to be detrapped.[53]

An important factor that affects the lifetime is the encapsulation. An organic light-emitting device exposed to air is degraded in hours due to the oxidation. An encapsulation in an inert atmosphere has to be used in order to protect the device from oxygen and humidity diffusing into the layers. The drawback of efficient encapsulation is the increased weight and the reduced flexibility of the device.

4.2 Brightness

The operation of an organic light-emitting device is mainly observable through the reduction of light intensity as a function of operation time (the higher brightness leads to the faster intensity reduction). The brightness level is inversely proportional to the lifetime. For organic light-emitting devices, the lifetime is strongly linked to the power efficiency and thus to brightness level. High brightness yields in a deteriorated lifetime and vice versa depending on the current density. The achievable brightness level from an OLED is very high; more than 100,000 cd/m^2 have been obtained from PLED.[54] OLEDs have been reported to have the lifetime of more than 100,000 h when producing a luminance of 100 cd/m^2 which is equal to a desktop monitor.[51]

The difference of LECs compared to conventional organic light-emitting diodes

(OLEDs) is a high brightness at very low operating voltages broadly independent of the work functions of the electrodes.[22] However, due to the electrochemical nature of operation, the operating voltage is limited to the window of electrochemical stability of the materials used in the device. This is a limiting factor in the maximum brightness that can be achieved with LECs.[55]

In $Ru(bpy)_3^{2+}$ -based devices, the highest brightness reported was 400 cd/m^2 in blends with PMMA at 3V.[42] However, higher brightness was achieved at higher operating voltages at the expense of the device stability and efficiency.[40]

4.3 Color

Color for SMOLEDs is obtained by using doping. Virtually any color can be obtained with this method.[56-58] In doped SMOLEDs, emitting layers transport electrons or holes and efficiently transfer energy to the luminescent dyes. Separation in functionality between molecules allows for greater flexibility in SMOLED design.

With regard to PLEDs, through chemical variation of the side chains of substituted PPVs, the energy gap can be tuned resulting in blue, red and green light emission.[59,60] Covion reported poly(p-phenylenes) (PPPs) for blue emission. Due to the fact that the technology is based on soluble polymers, they had to find a new way to cope with the inherently insoluble PPP for the blue emission.[61]

In LECs based on the conjugated polymer, the principle of color tuning is similar to that in PLEDs. Furthermore, LECs can tune color by different bias. With regard to LEC based on $Ru(bpy)_3^{2+}$complex, the red light has been proven. However, because of the limitation of energy gap of $Ru(bpy)_3^{2+}$ complex, it is not possible to get green and blue light. For display applications, we can choose the other organometallic complexes to match the requirement of full color display.[62,63]

Generally speaking, blue materials are not as strong as their red and green counterparts, fading sooner and limiting the utility of organic light-emitting devices for display applications. Since lifetime depends on color, this can pose problems for full color display degradation.

4.4 Luminescent efficiency

In accordance with Snell's law, when light passes from a medium of high refractive index to one of lower index, there exists a critical angle of incidence (the angle between the light propagation direction and the perpendicular to the surface) beyond which the light is totally internally reflected. Thus, a great deal of the light generated by an organic light-emitting device is trapped inside and waveguided out to the sides; this is normally about 80% of the total.[64)]

The efficiency of an organic light-emitting device is also affected by several factors: the degree of balance of charge carrier injection, the efficiency of recombination, and the efficiency with which the excited state emits light (the photoluminescence efficiency).[58)] Recombination efficiency is generally at or near unity if two charges are guaranteed to annihilate. However, if the annihilation process has no quenching, then quantum spin statistics dictate that only 25% of the resulting excited states will be useful emissive ones if the state has singlet multiplicity.[65,66)] Although emission from the triplet state is spin forbidden in ordinary organic molecules, the emission from transformation enabled by transition metal complexes containing at least one atom of higher atomic weight (which facilitates the triplet-singlet interchange called intersystem crossing).[30,48,67)]

In SMOLED, the emphasis has been on finding additives that can accept energy from the triplet excitation sites (which must provide the charge transport) and radiate with high efficiency.[56,68)] In PLED, the conjugated polymers are considered to hold a better quantum efficiency due to the formation of intra-chain singlet excitons.[54)]

In LEC, because there exists a balanced charge injection, the high efficiency can be achieved. In $Ru(bpy)_3^{2+}$-based device, $Ru(bpy)_3^{2+}$ complexes show a strong absorption band at 452 nm due to a metal to ligand charge transfer transition and the excited triplet state can be populated from an excited singlet state by intersystem crossing.[69-71)] Usually the efficiency of the electroluminescence is proportional to the product of the photoluminescence quantum yield and the efficiency of the production of excited states.[72,73)] Therefore, these complexes have high external efficiency and make them eminent candidates for applications of organic light-emitting devices.

4.5 Power efficiency

The fundamental quantity important to the user is power efficiency, since this determines how long the battery will last in a portable device. The definition of power efficiency is the ratio between the power and the amount of emitted light. For organic light-emitting devices, the power efficiency is of great concern due to that an improved efficiency leads to a better lifetime. The power efficiency is similar to the external quantum efficiency. The external efficiency includes the internal efficiency but also takes the factors such as light emission from the side of the device and internal refraction into consideration. Internal quantum efficiency is defined as the amount of emitted photons in comparison to the amount of electrons injected into the emitting layer. The internal quantum efficiency for organic light-emitting devices depends on the electron-hole recombination in the emitting layer, where an increased amount of recombination leads to a better efficiency. It is therefore important to choose a material with good recombination property. The other consideration about increasing efficiency was in Sub-section 4.4.

Power efficiency is measured in lumens per watt. (The lumen is a measure of luminous power, scaled to the sensitivity of the human eye; thus there are more lumens per watt at the sensitivity peak of 555 nm than at a wavelength in either the red or blue region.) Incandescent light bulbs used in the home range from about 10 – 15 lumens/watt; fluorescent bulbs can be as much as 80. Currently the best OLEDs are achieving in excess of 20 lumens/watt (for green), although many devices are well below this (often only a few lumens/watt).[74] Progress in improving this number has been rapid during the last few years and will doubtlessly continue; in fact, while it is a long range goal, the use of organic light-emitting devices for general illumination may be proved feasible.

Power efficiency is affected not only by the external quantum efficiency of the device (number of photons out per electron in), but also by the voltage at which the device operates. According to Ohm's law, power is the product of current and

voltage. Thus, it is important to obtain low operating voltage which is related to the charge injection barrier. Low voltage is also desirable to provide compatibility with batteries. Voltages for the systems likely to see early application are around 3-6 volts.

4.6 Advantages and drawbacks

Table 1 enumerates the performance of OLEDs and LECs that emit red light.

Table 1 Comparison of different organic red light-emitting devices[a]

	SMOLED	PLED	Polymer LEC	$Ru(bpy)_3^{2+}$ - based device
Voltage (volt)	10.6[75)]	2.8[78)]	2.5[79)]	2.4[40)]
Brightness (cd/m^2)	100[76)]	100[78)]	100[79)]	50[40)]
External quantum efficiency (%)	2.2[76)]	2.1[78)]	2.5[79)]	6[40)]
Power efficiency (lm/W)	0.6[76)]	3[78)]	-	4.1[40)]
Life Time (hr)	10,000[51)]	>8,000[76)]	100[80)]	1000[40)]
Response Time	<1ms[77)]	1.5ms[77)]	10ms[79)]	1s[40)]
Color	red, green, blue	red, green, blue	red, green, blue	red
Production	vapor deposition	spinning coating, ink-jet printing	Spinning coating, ink-jet printing	spinning coating, ink-jet printing

[a]Emitting color is red, except polymer LEC whose light is orange.

Satisfactory performance for indoor and portable display applications requires a brightness of around $100cd/m^2$ at an operating voltage between 5 and 15 volts and a continuous operational lifetime of at least 10,000 hours.[9)] The performance parameters for the comparison are illustrated in Appendix 1.

In the practical application, the two classifications of OLEDs have their drawbacks and advantages and the industry has not yet agreed upon which one that is best suited as an industrial standard. SMOLEDs are believed to have a leading position due to the earlier discovery. PLEDs are considered to possess a higher power

efficiency compared to the small molecules due to better internal efficiency of the emitting layer.[54] Through doping of the small molecule materials the efficiency can be enhanced.[68] Another considerable difference between the two material groups is the manufacturing method. SMOLEDs are manufactured through vacuum evaporation. PLEDs are spin-coated, which is cheaper than evaporation. To accomplish the best features of an organic light-emitting device, a combination of the two classes is the best approach.

Electrochemical cells have some advantages over traditional OLEDs since LECs operate independently of the work function of the electrodes, lower operating voltage and have a more balanced charge injection, which makes one layer sufficient for high device efficiency.[81] From Table 2, there is a significant decrease of the voltage from 10.6V in SMOLED to 2.4V which is required for $Ru(bpy)_3^{2+}$-based device. In the LECs, the p-n region which makes low-resistant contact of organic layer and electrode are formed by electrochemical doping in the organic layer. Thus, light emission can be observed in forward and reverse bias, and the onset voltage is almost independent of the layer thickness.[13,82] However, because ions have to redistribute in the device prior to the charge injection, the response time of such devices is slow. Depending on the mobility of the ions and the applied voltage, the delay time can be in the range of seconds to minutes. This delay time is one of disadvantages of LECs because a fast switching time (before the human eye notices any flicker which is typically about 70 times per second) is required for typical display applications. Moreover, the lifetime of such devices has scarcely been qualified and thus seems not to be competitive with OLEDs.

In LEC based on the conjugated polymer, one approach to solve slow response was achieved by frozen-junction LEC which means freezing out the ion motion after p-n region is formed.[83-85] In a first step, p-n region is created at an elevated temperature (where the ion mobility is high), while at the lower operating temperature (where the ion mobility is negligible so the doping profile and the p-n junction are stabilized). Such devices show the typical characteristics of PLEDs such as unipolar light emission to avoid cross-talk in column-row addressable display and a fast response

time.[86]

The other problem of polymer LECs is phase separation. Heeger and co-workers included a bifunctional liquid additive to the electroluminescent layer to stabilize the polymer network.[79] The other way to avoid phase separation is to fabricate the conjugated polymers which provide electroluminescent and charge transport properties.[87] Finally, the best way is to combine luminescent and ionic properties in a single polymer without any additives.[88]

In comparison to polymer LECs, $Ru(bpy)_3^{2+}$-based devices have the advantage that mobile ions are already present in the structure and therefore no additional phase with an electrolyte and a salt is necessary. With regard to response time, the judicious choice of the counterions or by using pulsing schemes, this time can be reduced dramatically.[34,40] Ru(II) complex is chosen for its high efficiency in a device and good film forming characteristics during spin coating due to blending with glassy polymers such as PMMA which also dilute the complex to reduce concentration quenching.[40,42] Thus, the devices might offer the requirement in the industrial view discussed previously because of their characteristics of high efficient elecotroluminescent property and solution-based operation that spinning coating is available.

5.0 Intellectual property

In two types of light-emitting diodes, early research was focused on SMOLEDs which have a head start over PLEDs. Much of pioneering work in this field was done by Kodak, which has made a number of major breakthroughs and has patented some of the basic materials and techniques for OLED manufacture. Lately, various companies, such as Cambridge Display Technology, DuPont, Covion, and Dow Chemical have been developing technologies for PLEDs.

In the light-emitting electrochemical cell (LEC), Uniax Corporation reported the remarkable LEC based on a conductive polymer first in 1995. Polymer LECs have important advantages over PLEDs. For example, the way in which electrical charge is injected into the conductive polymer is independent of the work function of electrodes, and the performance of LECs is insensitive to the thickness of the material.

The investigation below is intended to identify development of intellectual property of the dominant companies and their potential to block the technology of $Ru(bpy)_3^{2+}$-based device in the field of organic light-emitting devices. The information about each of the patents has therefore no intention to be complete.

5.1 Patents on SMOLED

Kodak (Chang and Van Slyke) was the original inventor of small-molecule electroluminescence. Since then, Kodak researchers have made a number of major breakthroughs which led to patents on basic OLED materials,[89] device structures,[90] doping techniques to drastically improve efficiency and control color,[91,92] thin-film deposition methods,[93] patterning methods,[94] as well as designs and fabrication methods for both passive and active-matrix OLED panels.[95] Now the company holds more than 40 U.S. patents. Today, the materials developed by Kodak are licensed to eMagin, Sanyo, Pioneer, TDK and Nippon Seiki.

Universal Display Corporation (UDC) is active in the development of innovative small-molecule organic light-emitting device technology for future generations of flat panel displays, lasers and light generating devices. Universal's

development of phosphorous OLEDs has introduced a possible alternative branch to Kodak's small molecule fluorescent OLED. Since its founding in 1994, UDC has collaborated with world-renowned researchers from Princeton University and the University of Southern California to develop leading-edge OLED technology. UDC has the worldwide, exclusive license rights to develop, manufacture and market products, and sublicenses those rights based on their patents in this area. UDC has built an intellectual property portfolio that contains over 100 issued U.S. patents. Intellectual property includes the use of electrophosphorescent emitters,[96] and transparent,[97] flexible and stacked OLEDs.[98,99]

In the area of blue-emission technologies, Idemitsu Kosan employs vapor deposition of a high-luminescence, high-efficiency, long-life organic blue-emission material to create an ultra-thin film.[100] The result is a material capable of emitting blue light with a high degree of brightness and of achieving the high emission efficiency while requiring only a low voltage.[101] For full-color implementation, Idemitsu Kosan uses the combination of a blue mono-color emissive-layer display, and a proprietary color conversion technology.[102] Specifically, the panel incorporates a color conversion material that transforms blue emission into green and red. This material is patterned in front of an organic blue electroluminescence display.

5.2 Patents on PLED

Cambridge Display Technology, CDT, is the initial developer of light-emitting polymers (LEPs) and is now leading industry to make an effort in their research and commercial development. These unique, light-emitting compounds are being developed for a broad range of existing and emerging display applications. CDT has a patent portfolio of around 100 patent families covering LEP device architectures and LEP materials.[103,104]

DuPont Displays, a unit of DuPont iTechnologies, is a business focused on the display market for devices such as cell phones, personal digital assistants and notebooks. As part of DuPont, the long established scientific innovator responsible for some of the world's most famous materials, a wealth of technological and

development resources are quickly available through a worldwide network of research centers and experimental stations. Dupont has merged Uniax which has strong manufacturing patents for PLEDs.[105] Based on DuPont's core expertise in polymer science, DuPont materials experts are at work on the intellectual property which improves plastic and polymer materials to form the substrate of displays.

Covion is based in Frankfurt and specializes in advanced material solutions and technologies for displays and electronics of PLEDs. Recently Covion has achieved a breakthrough in development of electroluminescent (EL) polymers for high-efficiency full color displays. It makes feasible the robust and efficient high resolution patterning processes for EL polymers using photolithography.[106] It links the ease of PLED device manufacturing by solution processing (e.g. spin coating) with an established patterning process (photolithography) to enable the manufacture of high resolution PLED displays. These have been shown to retain the efficiency, color and stability expected of conventional PLED devices.

The Dow Chemical Company had been working to develop polymers for use in PLED displays. Dow has intellectual assets related to polyfluorenes, as well as the process and scale-up knowledge.[107-109] This company is focussing on PLED materials development, performance and scale manufacturing.

5.3 Patents on LEC

Uniax corporation owns the shiny polymer known as light-emitting electrochemical cell (LEC). There are six patents about LEC issued from this company. Some of them claim that electrochemical light-emitting devices with a composite material between two electrodes.[110-112] The composite material is a mixture of ionic species, a conjugated polymer and a high-boiling gel-forming liquid. The presence of high-boiling gel-forming liquid improves the efficiency of the devices. The conjugated polymer is capable of supporting both p- and n-type carriers and having a doping profile which can be dynamically changed in a controlled fashion through reversible electrochemical oxidation and reduction. Devices having this structure may be used to generate electrochemically induced p-n junctions, thereby

providing a new means of exploiting the light-emitting properties of such junctions under an applied voltage. The others claim that the addition of a highly polarizable additive such as an organic anionic surfactant to an electrically active polymer improves the electrical properties of the polymer.[113-114] When such an additive is added to an electroluminescent organic polymer, this mixture can be used in diodes having a transparent anode and an air stable metal cathode having a work function larger than 4eV. The external efficiency and brightness versus voltage are significantly improved compared to results obtained with the same electroluminescent polymer used alone with high work function (>4.0eV) metal cathodes.

The other patents related to light-emitting electrochemical cell use conjugated polymers as emissive layers. One issues the novel conjugated polymers comprised of arylamine-substituted poly(arylene vinylene).[115] The characteristcs of this conjugated conjugated polymers are soluble in common organic solvents and can retain semiconductivity and electroluminescent efficiency. The others relate to electroluminescent polymer compositions and processes for the preparation in light-emitting electrochemical cells. The invention is the process for preparing soluble poly(arylene vinylene) polymers.[116,117]

With regard to light-emitting devices related to ruthenium complexes. The patents are about the use in the manufacture of conjugated polymers. For example, one patent claims that the catalyst of ruthenium complex can be used to synthesize cyclooctatetraenes as electron transporters in organic light-emitting diodes.[118]

Overall, the patents in light-emitting electrochemical cells specify that the emissive layers must be conjugated polymers such as various polyarylene vinylenes. With regard to the patents related to ruthenium complexes, the applications concentrate on catalysts used to synthesize the materials for organic light-emitting diode. Consequently, there is no patent to block the technology of organic light-emitting device based on $Ru(bpy)_3^{2+}$ complex. Therefore, the present patents cannot prohibit the practice of the technology of $Ru(bpy)_3^{2+}$-based device.

6.0 Economic analysis of $Ru(bpy)_3^{2+}$-based device

6.1 Introduction

Recent advances in the production of light from organic materials have led to intense activity in universities and companies across the world. The advantages promised by the technology of light-emitting devices include:

(1)Thin, lightweight, printable displays
(2) Low voltage, low power, emissive source
(3) Good daylight visibility through high brightness and contrast
(3) High resolution
(4) Broad color gamut
(5) Wide viewing angle
(6) Low bill of materials

These features make this technology attractive in display and lighting industries. Organic light-emitting devices are expected to grow rapidly. In 2005, OLED market will reach $2.7 billion (Display Search). It is estimated $112 million market size today (Stanford Resources). The key industries for OLED display are automotive, cellular phones, consumer electronics and others.

One of the strategies in the early stages of the technology for commercialization is to build the cost model because it is a real amount, unlike resources, which are hard to define and measure. As the issues in the cost model are understood and the paths to production and commercialization become clearer, we can evaluate the state of technology and the value of research direction.

6.2 Cost analysis and capital requirement

The exact cost model is difficult to accurately predict prior to the design phase; however, it is possible to figure out the design process and to achieve an adequate relative cost model. In order to model the moderate cost, we break down the cost and then add them together to give a total cost.

Materials:

Light-emitting devices based on ruthenium complex are prepared by spin coating with the acetonitrile solution which is blended with PMMA (25 vol. %). The final emissive layer has a thickness of 1200Å. Although there have been many efforts to identify an alternative transparent anode material, ITO has most of the desired properties for organic light-emitting devices on glass. In OLEDs, it is important to match work function of cathodes to the LUMO (the lowest unoccupied molecular orbit) levels of the organic layer, but we can use silver (Ag) as the cathode which is the air stable material in $Ru(bpy)_3^{2+}$-based device.

Encapsulation is critical for organic light-emitting devices. Achieving good sealing will perhaps depend more on the adhesion of the sealant to the glass or metal than on the bulk permeability of the sealant material. The incorporation of desiccants is essential to raise the tolerance for ingress influx as well as to soak up water or oxygen that desorbs from the material inside the device after sealing. The design and manufacture of IC drivers remains a matter of concern, especially with regard to cost.

The costs of materials are listed in the Table 2.

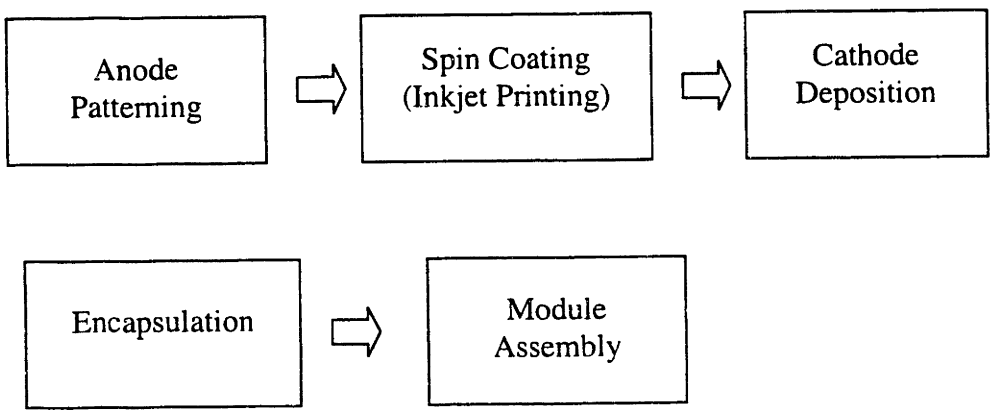
Table 2 Costs of raw materials[a]

Material \ Cost	$/Kg	$/in^2
Ag	256	1.73E-04
$Ru(bpy)_3^{2+}$	41700	2.00E-01
PMMA	3	1.80E-05
Acetonitrile	12.5	2.50E-03
ITO substrate	-	2.50E-03
Module materials[b]	-	2.00E-02
	Total	1.30E-01

[a] Quantity of polymer solution for spinning coating: 0.21ml/in^2.
[b] Module materials include electronics and encapsulation materials.

Processes:

The process of manufacturing of $Ru(bpy)_3^{2+}$-based device is shown in Scheme 1. $Ru(bpy)_3^{2+}$-based device has the advantage that it can be deposited



Scheme 1 Manufacture Process of $Ru(bpy)_3^{2+}$-based device.

from a solution, allowing low cost processing methods such as spin coating and even roll-to-roll processing, instead of chemical vapor deposition. In the spin-coating process, once the film has been thinned by spinning the substrate, it is solidified by

heating. Control of film composition and thickness uniformity to dimensions are required in OLEDs which are problematic by spin-on techniques. However, $Ru(bpy)_3^{2+}$-based device allows standard polymer thin film processing technologies such as spinning coating, painting and dip coating because the turn-on and operating voltages of the LECs are not sensitive to the thickness of the film. While the application of the organic layers occurs by such potentially low-cost solution-based process, a metal cathode must still be vacuum deposited.

Organic materials are vulnerable to contamination by oxygen and water vapor, which can trigger early failure. The present practice of fabricating the OLED on glass and covering with a metal can is regarded only as a short-term expedient. In many cases the cover will be a second glass sheet. Improved materials are needed as sealants at the panel edge and as desiccants to absorb water or free oxygen that is left over from fabrication or seeps in encapsulation.

6.3 Cost model conclusion

Figure 11 is the result of cost analysis. The detail information about cost

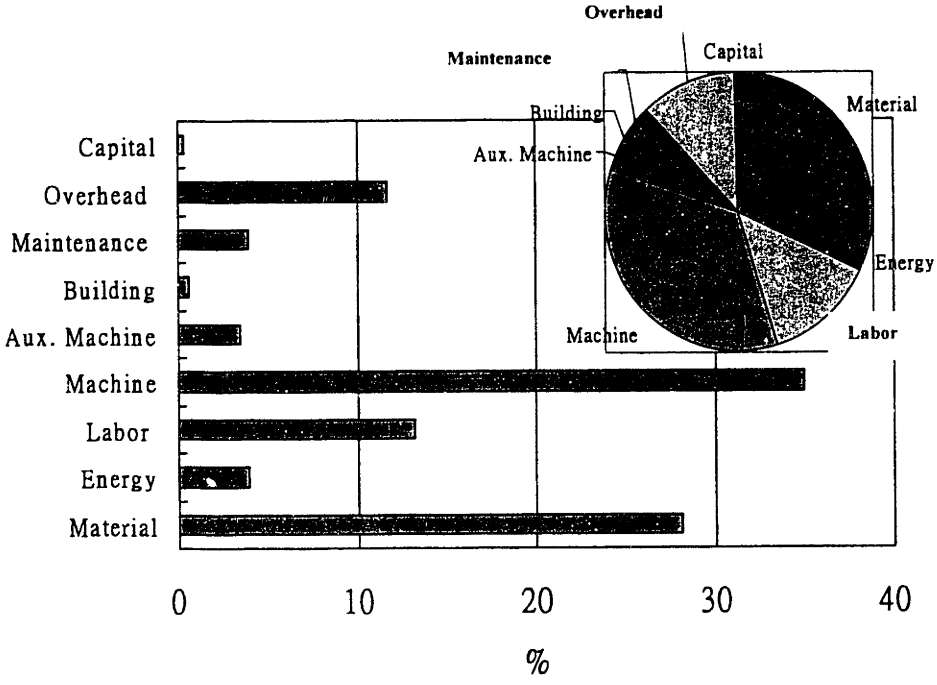


Figure 11 Cost estimate of $Ru(bpy)_3^{2+}$-based device.

analysis is shown in Appendix 2. It is intended to construct a 300 square-meter factory. The land cost is $330,000; the main equipment will cost around $14,285,000 and the three-floor building cost $128,400. Inclusive of running costs, the total initial investment would be around $22,000,000. This will cover all capital investment and running costs for one full year.

Basically, the display business is an area business; therefore, it is decent to express the cost in the unit of square inch. The cost of $Ru(bpy)_3^{2+}$-based device is $1.54 per square inch. As to the cost issue, DisplaySearch published a comparison between LCD and SMOLED for a 15" XGA display. The costs of LCD and SMOLED are $3.16 and $1.82 per square inch respectively. The results show that the cost of $Ru(bpy)_3^{2+}$-based device is lower than those of LCD and SMOLED. Organic light-emitting devices may have a cost advantage depending on yields due to the elimination of numerous materials such as the color filter, liquid crystal and backlight. The reason that the cost of $Ru(bpy)_3^{2+}$-based device is lower than that of SMOLED might be the simple composition of the organic layer and low-cost coating process. In the selling price in different products, the average prices are above two dollars (Table 3). That means using the technology of $Ru(bpy)_3^{2+}$-based device can achieve a high profit. However, there are some problems mentioned before (Section 4) in $Ru(bpy)_3^{2+}$-based devices such as full-color ability, short life time and long response time. In practice, we can select the monochromic market of PDA and backlight to enter first, then continue to work on the improvement of performance of $Ru(bpy)_3^{2+}$-based device. In the aspect of diffuse light sources, the removal of the need to create small pixels and the associated circuitry for switching substantially eases the problems such as fine patterning, contrast, pixel switching and color saturation. Besides, the facilities used in the production of display devices might be used to fabricate lighting devices; it is helpful to increase the multiplicity of the function of equipment and thus reduces the equipment depreciation. The bottom line of implementation for reducing the power consumption of lamps installed in homes and business by organic light-emitting devices is that additional government funding can be available to stimulate such work.

Table 3 Average Display Prices[a]

Display \ Year / Price	2003	2004	2005	2006
Cellular Phones (TFT color)	9.3	8.5	7	6.8
Cellular Phones (STN color)	5.8	5	4.2	3.7
Cellular Phones (STN mono)	3.5	3	3.1	3
Portable Computers (14-inch TFT color)	2.2	2	2	2

[a]Unit of price, $\$/in^2$.

In brief, the developing process of a new technology will take a long term vision, patient capital, radical innovation in both technology and marketing. Nonetheless, $Ru(bpy)_3^{2+}$-based device is still a concept with enormous appeal in the view of organic light-emitting devices.

7.0 Conclusion

Light-emitting devices based on the $Ru(bpy)_3^{2+}$ complex and its derivatives have the potential to combine good device performances with simple device manufacturing techniques. The devices are between SMOLED and PLED. The electroluminescent material is $Ru(bpy)_3^{2+}$ complex and the manufacture is similar to the process of PLED which is available to use coating technology. Therefore, it is possible to produce large-area display and to reduce cost compared to SMOLED fabrication which needs to deposit as thin films by the relatively expensive techniques of sublimation or vapor deposition which are not well suited to fabrication of large-area displays as well. $Ru(bpy)_3^{2+}$complex is a charged, phosphorescent small molecule that can be processed into single layer devices by spinning coating using stable cathode materials such as Ag or Al. No elaborate film fabrication or "charging" schemes are required, and no reactive cathode materials (e.g. Ca, Mg) are needed. Therefore, such devices might become attractive to commercial applications such as backlights for displays used in watches, cell phones or toys.

However, a substantial disadvantage with this new technology is that it has not yet proved a lifetime sufficient for the display demands of the market. This was found in the paper study (Section 4). When and if the problem of the lifetime will be solved, this kind of organic light-emitting device will surely be favorable to the commercialization. The short lifetime of $Ru(bpy)_3^{2+}$-based device is caused by the degradation of emitting material. The two main contributors to the degradation process are a high current density and bad encapsulation of the organic layers. The degradation was dramatically slowed at low voltages, suggesting that it is current induced. It should be mentioned that pulsed driving schemes can be used to mitigate this degradation. Besides, some of the most important requirements for $Ru(bpy)_3^{2+}$-based devices such as a good shelf life in the on- and off-state, a low operating voltage, high efficiency, brightness and a fast response time remain to be improved.

The concepts for light-emitting electrochemical cells based on the $Ru(bpy)_3^{2+}$ complex might be transposed to other charged phosphorescent material systems. The

use of different emissive materials would introduce different colors and has the potential to lead to higher quantum efficiency or faster response time. There are vast numbers of phosphorescent transition metal complexes which could be tested for their use in light-emitting electrochemical cells. Furthermore, similar to OLEDs, it is possible to add small amount of a phosphorescent dye into this system. This would not only improve the efficiency by avoiding concentration quenching but also allow color tuning of the emission spectrum.

Given the presence of many groups in the effort of LEC technologies, in both industry and academia, and the rapid progress being made by OLED, it is beneficial for the technology of $Ru(bpy)_3^{2+}$-based devices to cooperate with display manufacturers to develop the unique intellectual property. It has to take care of the criteria for display requirement in the long run.

The development of the technology of $Ru(bpy)_3^{2+}$-based devices is still in its infancy, however, the simple design and excellent properties make them a promising candidate for commercialization potential.

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Appendix 1 Definition of performance parameters

Brightness (cd/m^2)

the luminous intensity divided by the surface area of the light source

unit of luminous intensity: candela (cd)

1 candela is defined as 1 lumen per steradian (lm/sr)

Luminous power P_l (lumen)

$$P_l = P_r \cdot p_{(\lambda)}$$

$p_{(\lambda)}$, *conversion factor (lm/W) (Figure 1)*

A steradian is defined as conical in shape (Figure 2). Point P represents the center of the sphere. The solid (conical) angle q, representing one steradian, is such that the area A of the surface portion of the sphere is equal to r^2, where r is the radius of the sphere.

External quantum efficiency η_q (%)

the percentage of photons per electron can be found in the given radiometric power and the electrical current,

$$\eta_q(\%) = \frac{\#\,photons}{\#\,electrons}(\%) = \frac{P_r \cdot \lambda}{hc} \cdot \frac{e}{I} \cdot 100\%$$

I: the current passing through the device (A)
Pr: the power emitted by a light source (W)
h: Planck's constant
c: the speed of light
λ: the emission wavelength

Power efficiency (lm/W)

the ratio of the luminous power P_l emitted by the light source divided by the electrical power required operating the device

$$\eta_{Pl}\left[\frac{lm}{W}\right] = \frac{P_l}{I \cdot V}$$

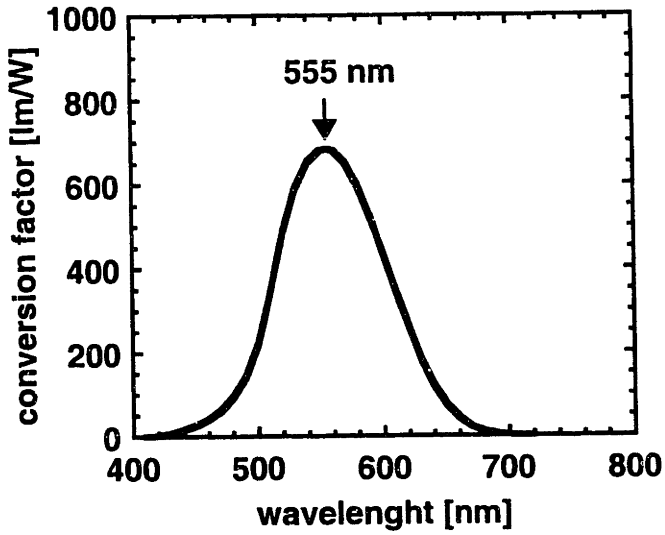

Figure 1 Conversion factor vs. emission wavelength. At 555 nm, 1 W radiometric power is defined as 683 lm luminous power.

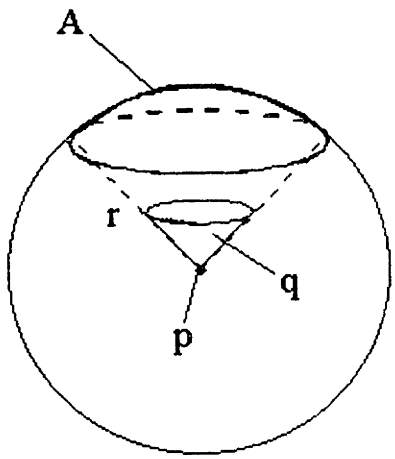

Figure 2 A cone with a solid angle q, that has been removed from a sphere with its vertex at the center of the sphere.

Appendix 2 Cost model of $Ru(bpy)_3^{2+}$-based device

$Ru(bpy)_3^{2+}$-based device - Analytical Technical Cost Model

EXOGENOUS DATA

Annual Production Volume	7,056,000	in^2
Direct Salary/hour	$11.84	
Working days/year	269	
Downtimes		
No Operations	1.5	hrs/day
Planned Paid	1.5	hr/day
Planned Unpaid	0	hr/day
Real Estate/Bldg	$1,000	/sq.m
Construction (330m^2*3Floors*$129.5)	$128,400	
Others (facilities in the Office, partition)	$57,000	
Bldg Recovery Life	20	yrs
Price of Electricity and Steam	$0.08	/kWh
Capital Recovery Rate	10%	
Working Capital Period	3	months
Life of Machine	5	yrs
Overhead Burden	30%	

Process Inputs

Unplanned downtime	1	hr/day
Scrap rate	5%	
Reject	15%	
Workforce/machine	21	
Related Equipment	10%	
Installation Cost	2%	
Maintainence Cost	10%	
Electricity/Steam Requirement	0.64	unit/in^2

Variable Costs

	per in^2	per year	percent
Material	$0.4000	$3,084,542.24	28.1%
Energy	$0.1000	$423,529.39	3.9%
Labor	$0.2000	$1,445,569.60	13.2%
Total Variable Cost	**$0.7000**	**$4,953,641.23**	**45.1%**

Fixed Costs

	per in^2	per year	percent	investment
Main Machine cost	$0.5400	$3,843,713.95	35.0%	$14,570,700.00
Aux. Machine Cost	$0.0500	$376,834.70	3.4%	$1,428,500.00
Fixed overhead cost	$0.1800	$1,284,326.20	11.7%	
Bldg. Cost	$0.0100	$60,538.69	0.6%	$515,400.00
Maintainence Cost	$0.0600	$428,108.73	3.9%	
Cost of Working Capital	$0.0044	$30,960.26	0.3%	
Total Fixed Cost	**$0.8444**	**$6,024,482.54**	**54.9%**	**$16,514,600.00**

Total Fabrication Cost	**$1.5444**	**$10,978,123.77**	**100%**

RELATED VARIABLES

Material Variables

Raw Material Price	0.353	$/in^2
Scrap Rate	5%	
Annual Material Input	8738080	in^2

Process Calculations

Effective Production Volume	8301176	
Available Operating Time	5380	
Paid Operating Time	5783.5	
Effective Cycle Time	4.60E-02	mins/in^2
Required Operating Time	5409.6	hours/year
Required Building Space	330	sq.m
# of Parallel streams	1	
Run time for One Machine	1.01	

Equipment and Machinery Cost

Facility	14285000	$

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