

# Commercialization Potential of Quantum Dot Light Emitting Devices

by

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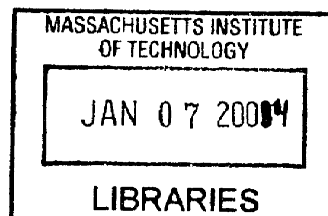
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## ABSTRACT

The use of quantum dots as discrete emitters in hybrid organic/inorganic light emitting devices is an attractive approach for producing novel display products. These structures exhibit narrow-band emission tunable across the visible spectrum - characteristics allowing for display devices not possible with current OLED materials. In this work, quantum dot light emitting devices (QD-LEDs) using small molecule host materials are evaluated as a potential platform for the growing OLED industry. Specific applications are suggested and the primary technology hurdles identified. A search of relevant patents pertaining to quantum dot synthesis and device structure was conducted to reveal a significant opportunity for the commercialization of QD-LED devices. A business model has been devised based upon several developing companies in the OLED industry with a focus on licensing of technology as the primary source of revenue.

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# CONTENTS

1.0 Introduction	5
2.0 OLED Technology	6
2.1 Historical Perspective	6
2.2 Description of a Heterojunction Device	8
2.3 Phosphorescing Dopants	11
3.0 Quantum Dot Light Emitting Devices	12
3.1 Dawning of a New Device Paradigm	12
3.2 Structure of the Quantum Dot	13
3.3 QD-LED Device Structure	14
3.4 QD-LED Device Performance	17
3.5 Further Work	18
4.0 Applications	20
4.1 QD-LED Applications	20
4.2 OLED Display Industry Background	22
4.3 Current Performance	27
4.4 Competing Technologies	28
4.5 Dendrimer Based PLEDs	31
5.0 Intellectual Property	32
5.1 QD and QD-LED Related Patents	33
5.2 Materials Technology Patents	36
5.3 OLED Processing Patents	37
6.0 Business Analysis	37
6.1 Business Model	37
6.2 Extended Business Plan	40
6.3 OLED Market Performance	42
7.0 Conclusion	43
8.0 References	45

## 1.0 Introduction

Research in the field of organic semiconductors and devices has witnessed tremendous growth over the past 50 years<sup>1</sup>, revealing new fields of study and many promising avenues for commercialization. From the discovery of electroluminescence in organic anthracene crystals in the 1960's to the awarding of the Nobel Prize in Chemistry (2000) for the "discovery and development of conductive polymers"<sup>2</sup>, organic materials have swiftly come to the forefront of scientific investigation. Nowhere does this appear more relevant than in the field of organic light emitting diodes (OLEDs). In recent years, research into these novel light-emitting devices has ignited the interest of academia and attracted the investment of significant capital and resources from industry<sup>3,4</sup>. Primary in their interests is the demonstrated potential of OLEDs as building blocks for advanced display applications. Indeed, recent advances in OLED and organic thin-film transistor (OTFT) technologies have shown tremendous promise in the flat panel display industry as both a disruptive element<sup>5</sup> to current LCD systems and as a platform for farther-reaching technology. Newly announced devices have exceeded the benchmark set by the LCD display industry with higher luminous intensities and lower power consumption<sup>6,7</sup>. The unique mechanical characteristics of organic films have also lead to the realization of flexible color display systems fabricated from plastic substrates; an idea that opens the door to an almost unimaginable range of display devices and new applications. It is certain that with continued development, OLED technology will result in more durable and higher quality displays that will drastically increase the functionality of the devices in which they are used.

However, with the natural amount of hype comes with it the reality that such technology is still well into the future. Research groups and commercial institutions remain faced with significant barriers that must be overcome for OLED technology to become a viable commercial product. Issues such as device lifetime, material stability and efficiency must be addressed. This study will examine several of these issues and will focus on how a particular new development combining organic materials and semiconducting nanocrystals may lead to better devices.

In section I, current OLED technology is discussed – from the underlying physics describing energy transfer and light emission to current fabrication techniques and structure. A method of improving the operating efficiency will be reviewed, namely the inclusion of phosphorescent doping materials in the light emitting region. Focus will be placed on small-molecule OLEDs although similar analyses may apply to polymeric-based devices.

Section II introduces a recent development in the progression of OLED device structure – the use of semiconductor quantum dots as discrete emissive layers. An overview of solution based formation of quantum-dot nanoparticles is given and is followed by a description of how these particles are implemented into active devices. Current research paths are identified along with the issues that remain unaddressed.

In section III a review of current applications of OLED technology is given along with a development path that has been proposed by the Universal Display Corporation (UDC). Current issues facing manufacturers and the potential of QD-LEDs as a viable technology are reviewed. Furthermore, the benefits and drawbacks of the primary competitive technologies (with a special note on dendrimer technology) are discussed.

Section IV examines the intellectual property field associated with QD-LEDs, listing relevant patents that have been issued and identifying those that may potentially block further commercialization. Several key actions that must be taken for the successful implementation of a QD-LED business are discussed. Section V concludes with a strategic model and business plan for a QD-LED startup along with current and projected market performance of the OLED industry.

## **2.0 OLED Technology**

### **2.1 Historical Perspective**

Research in the field of organic devices has steadily progressed since the early 1960's when it was observed that certain organic materials are photoconductive under visible illumination<sup>8</sup>. Proliferation of this discovery into such areas as xerography and liquid crystal displays was rapid and efforts to create active organic devices soon followed. Unfortunately, it became evident that organic materials are poor substitutes for

semiconductors in developing such devices as solar cells, light emitters, and thin-film transistors. Early light emitting devices, for example, required extremely high potentials on the order of 100V, resulting in very low power conversion efficiency<sup>9</sup>. This was primarily due to the low carrier mobilities in most organic materials and the tendency of these materials to preferentially transport one carrier type over the other. The inherent instability of organic materials and the difficulty in applying electrical contacts to their surfaces further limited the possibilities for organic materials. And furthermore, exposure to water vapor and air were seen to accelerate the degradation of their mechanical and electrical properties.

Many of these issues remained at large until 1987 when two researchers at Eastman-Kodak reported the fabrication of an efficient light-emitting device made from organic thin films. In their seminal work, Ching Tang and Steven VanSlyke<sup>10</sup> demonstrated a vacuum deposited device with high external quantum efficiency (1% photon/electron), high luminous efficiency (1.5lm/W) and a brightness of over 1000cd/m<sup>2</sup> at voltages below 10V. These early devices were fabricated using a class of synthetic dyes consisting of roughly 30-40 atoms covalently bonded to form stable molecules known as monomers. When such molecules are bound together through weak organic bonding, they form stable, bulk layers and serve as building blocks for the fabrication of small-molecule OLEDs. However, it wasn't until a similar discovery in 1990 of a light-emitting device using polymer-based materials by R. Friend and associates<sup>11</sup> at the University of Cambridge, that widespread interest began in the area of organic light emitters. Unlike the small molecule OLED, their device employed a semiconducting polymer film of poly para-(phenylene vinylene) (PPV) which was spin cast to form the active layers. The mechanical flexibility of these OLEDs sparked substantial interest from display makers, for their potential use as bright, self-emissive displays on bendable plastic substrates. Indeed, the prospect of such revolutionary display technology is a primary driver of OLED technology today.

The independent discoveries of small molecule and polymer-based devices have laid the groundwork for the dichotomy that exists in the OLED industry today. These two device schemes are the primary competing technologies and all subsequent material and structural advances have been based upon these two platforms. Although supporters of

both tracks will tout superiority of their technology, it is commonly acknowledged that small-molecule development is ahead of polymer based technologies by 18months<sup>12</sup>.

## 2.2 Description of a Heterojunction Device

Figure 1 depicts the typical structure of a small-molecule OLED. The first layer is composed of a thin transparent oxide such as Indium Tin-Oxide (ITO) over a glass substrate and serves as the anode, or hole injection contact.

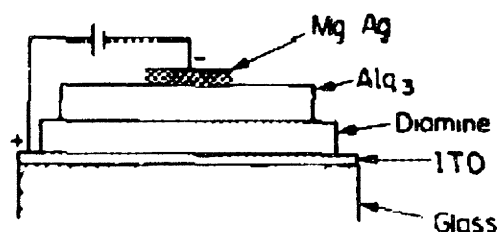


Figure1. Heterojunction structure of Alq<sub>3</sub>/Diamine OLED (From Ref. 10)

The first organic layer is then deposited over the oxide and is usually composed of a preferentially hole transporting material such as the TPD (N,N'-diphenyl-N,N-bis[3-methylphenyl]-1,1'-biphenyl-4,4'-diamine), an aromatic diamine. Because this layer serves to transport holes into the device, it is known as the hole transport layer (HTL) and is on the order of 500Å in thickness. An organic light emitting layer (LL) is then deposited over the HTL. This layer may also serve as the electron transport layer to which the device is then known as a single heterojunction structure. ETL layer materials usually fall under a group of metal-chelate complexes such as Alq<sub>3</sub> (which emits in the green) or Alq'<sub>2</sub>OPh (bis-[8-hydroxyl] quinalidine aluminum phenoxide, which emits in the blue. Effective electroluminescence has also been observed in double-heterojunction OLEDs which separate the LL and ETL into two distinct regions<sup>13</sup>. This is most effectively done by doping a portion of the ETL layer closest to the interface with a higher efficiency fluorescent or phosphorescent dye. A dual layer cathode is then evaporated over the combined LL/ETL layer. The first of these is a co-evaporated layer of Mg and Ag in a



nominal 25:1 mass ratio. Mg is co-evaporated with Ag to increase contact stability and retard oxidation and corrosion effects from the ambient. In addition, Mg is a low work function metal that serves to decrease the organic/contact Schottky barrier allowing for efficient injection of electrons into the ETL<sup>10</sup>. Ag also serves to improve the sticking coefficient of the electrode. A final Ag film is then deposited to form the cathode. Other material combinations include LiF/Al bilayers.

Patterning of the organic layers and contacts is currently limited to shadow masking, and to a lesser degree, the color-changing medium (CCM) approach<sup>14</sup> due to the incompatibility of traditional lithography techniques<sup>15</sup>. In shadow masking, a thin stencil mask with precisely defined aperture holes selectively shadows the vapor stream during the organic layer deposition in the vacuum chamber. For this technique to be useful, precise engineering of the shadow mask along with accurate alignment of the mask to the substrate are paramount. Research laboratories have successfully utilized this technique in developing devices, as have several major display manufacturers. Kodak/Sanyo has demonstrated active-matrix OLED displays with 50 $\mu$ m dot pitch while Pioneer Corp. has produced 5.2-in QVGA displays using the shadow mask method<sup>5</sup>.

Due to vastly differing carrier mobilities in each of the organic layer, OLEDs exhibit rectifying behavior with forward bias established with positive voltage applied to the ITO. Holes are injected from the anode into the HTL and electrons from the cathode into the ETL. Under the applied field, these carriers move toward each other and combine on a molecule to form a coupled electron-hole excited state, a state commonly known as an exciton. The region around the HTL/ETL interface in which this occurs is known as the recombination region and for an Alq<sub>3</sub>/TPD device is roughly 100 to 300 $\text{\AA}$  in width. The two-layer design is important because it provides the necessary energetic barriers at the interface to effectively localize the recombination of the oppositely charged carriers in the recombination region. Once an exciton is formed, the electron-hole pair may do one of three things: 1) recombine and release a photon 2) recombine in a quenching process whereby energy is dissipated non-radiatively, or 3) transfer its energy to another host molecule or species with a lower energy bandgap. If light is generated, the energy of the emitted photon will, in general, not correspond to the LL bandgap energy (the difference between the LUMO and HOMO levels of the emitting molecule) due to a "Frank-Condon

shift"<sup>16</sup>. The shifting of the emission spectra to a higher wavelength than the absorbed wavelength results in the transparency of the emitting layer to its own light and is one of the key benefits of organic thin films. In the case of Alq<sub>3</sub> whose spectrally determined bandgap energy is 2.7eV, the light output peaks at 530nm corresponding to the color green.

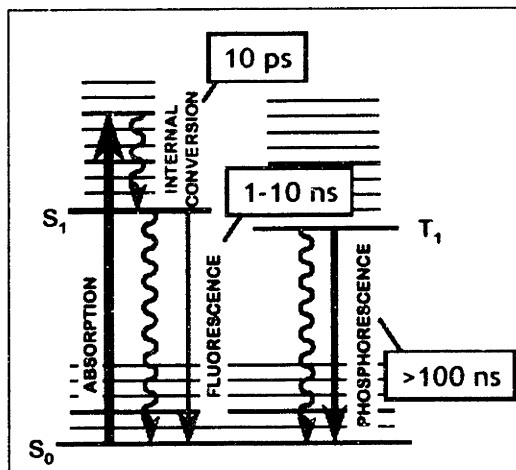


Figure2. Singlet and Triplet Relaxation phenomena (From Ref. 17)

Recombination of electrically pumped excitons must follow the spin conversion laws dictated by quantum mechanics<sup>18</sup>. In general, two exciton states exist – a spin symmetric triplet state with total spin  $S=1$  or a spin anti-symmetric state known as a singlet ( $S=0$ ). Because the relaxed ground state of an organic molecule is typically anti-symmetric, singlet excitons conserve symmetry in recombination and generate photons in an efficient process known as fluorescence. Relaxation from the triplet state is fundamentally not allowed but could take place if the excited singlet and triplet states partially mix due to the interaction with spin states of the nucleus. This phenomena is known as the spin-orbit coupling and is enhanced for molecules containing atoms with high nuclear number.

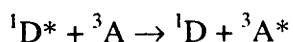
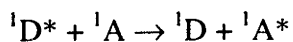
Unfortunately, due to the relatively long duration in which this recombination event tends to occur, triplet relaxation will most likely result in energy dissipation in the form of heat or other non-radiative mechanisms. Emission of a photon from triplet relaxation is possible in the form of phosphorescence, but is typically an inefficient process. Both singlet and triplet processes are shown in figure 2. The left side of the figure depicts the singlet transition with absorption causing an increase in electron energy from the ground

state  $S_0$  to an excited state above  $S_1$ . Spin symmetry in recombination results in fluorescence, a fast process occurring on the order of nanoseconds. The less efficient phosphorescence phenomena is shown in the right portion of the figure, with the resulting anti-symmetric relaxation from the  $T_1$  state to the  $S_0$  state occurring on the order of microseconds. It has been shown that the probability of forming a triplet state is three times greater than for a singlet state in electrically pumped organic materials. As a result, internal quantum efficiency for fluorescent heterjunction OLED devices is theoretically limited to no more than 25%. Furthermore, photoluminescence studies have shown that for  $Alq_3$  based devices, only 40% of generated singlet excitons recombine radiatively. Indeed common external quantum efficiency values for heterojunction structures hover around 1-2%.

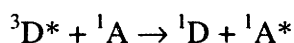
### 2.3 Phosphorescing Dopants

To increase the efficiency of OLED devices, radiative triplet recombination should be incorporated into the light emitting process. One way this may be achieved is by introducing phosphorescing dye molecules into the recombination region that effectively combine triplet and singlet relaxation modes<sup>19</sup>. The advantages of such a design are two-fold: by isolating photon generation onto a phosphorescing acceptor molecule, internal quantum efficiency may theoretically approach 100%. In addition, by reducing the excitation lifetime of the host molecule, the longevity of the device can be increased<sup>20</sup>.

The first of these conditions is requisite upon the efficiency of energy transfer between host and phosphor – which occurs if the emissive spectrum of the host molecule overlaps sufficiently with the absorption spectra of the acceptor. For example, the phosphorescing dye PtOEP exhibits an absorption peak at 530nm corresponding to the peak emission of  $Alq_3$  and thus is well suited as a dopant for  $Alq_3$  devices. Once significant spectral overlap has been established, energy transfer between host and dopant molecule can be accomplished in two ways. The first of these processes is known as an induced dipole or Förster energy transfer and is characterized by spin-conservation for both host (D) *and* acceptor (A). The allowed transitions are

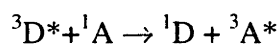


where the subscripts 1 and 3 indicate singlet and triplet states respectively, while “\*” indicates an excited state of a molecule. In Förster transfer, the triplet-singlet transition is in general not allowed.



Förster transfer is a relatively long range phenomena with an effective transfer distance of  $>50\text{\AA}$ . The level of doping of the host material, however, may influence this distance.

In order for energy transfer to occur from a host triplet state to an acceptor, direct electron wave function overlap must occur between the transferring molecules. This process is known as Dexter transfer and is a short-range process covering roughly  $10\text{\AA}$ . Unlike the Förster transfer process, only the total spin of the participating species must be conserved. Thus the doubly forbidden transfer,



is allowed meaning both singlet and triplet states may occur. When Dexter processes occur in parallel with Förster transfer, complete and efficient energy transfer is accomplished between host and acceptor, with rates reaching  $>90\%$ . Finally, for efficient photon generation to occur in the phosphorescent acceptor, the dopant must facilitate singlet-triplet intermixing via spin-orbit coupling. Such is the case for organometallic compounds having a heavy metal core as in PtOEP which exhibits quick and efficient electrophosphorescence on the order of (100ns-100 $\mu$ s).

The increase in external quantum efficiency for devices utilizing a phosphorescing dopant is dramatic with claimed values reaching 65, 10, and 4cd/A for green, red and blue respectively. According to a recent press release by Dupont Displays<sup>21</sup>, such efficiencies are close to the theoretically achievable limit.

### 3.0 Quantum Dot Light Emitting Devices

#### 3.1 Dawning of a new Device Paradigm

Research groups and commercial OLED developers worldwide have employed the techniques described above to create highly efficient, luminescing devices demonstrating excellent color output and performance<sup>22</sup>. Indeed, the cutting edge in small molecule OLED technology has its foundation in the use of these highly efficient phosphorescing

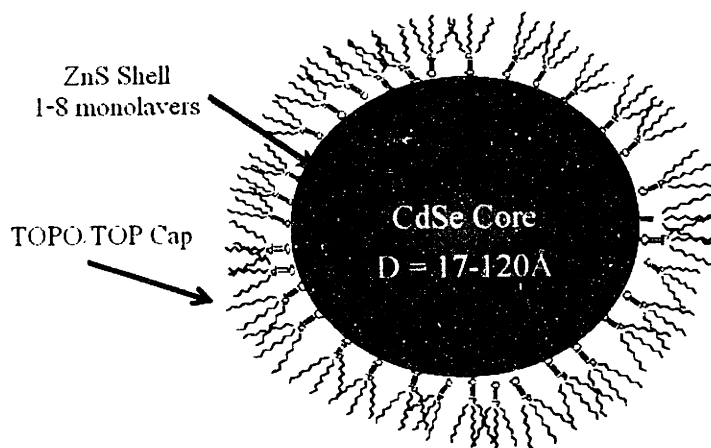
dopants and this technology will undoubtedly play a significant role for the production of future OLED display systems. Yet even as further advancements occur in phosphorescing materials research, there appears to be a fundamental limiting factor characteristic of this technique – that different dopant molecules must be used to tailor the output color of the device. Nearly all organic dopants have been shown to exhibit different rates of efficiency loss with use – a serious problem that has been one of the primary research foci of leading OLED developers. It is the primary reason why full color OLED display lifetime is currently so low. Furthermore, development of efficient light emitting organic molecules is still a costly process and results in high material cost for device manufacturers and the need for an array of chemical species on hand for the fabrication of multi-colored devices. Not only would it be more cost efficient if a single chemical platform could be devised that would allow for precise tuning of device color output, further development of such a device would be significantly faster and could potentially be immune to differential aging effects. Such a versatile, color tunable device platform is thought to exist - through the incorporation of semiconductor nanocrystals, or quantum dots (QDs) in active organic substrates.

### **3.2 Structure of the Quantum Dot**

A relatively new class of materials, semiconductor QDs are complex spherical structures with tunable radii between 10-60Å – sizes comparable and somewhat larger than typical organic molecules used in OLEDs<sup>23</sup>. QDs are further characterized by their strong quantum size effects; the absorption and emission profiles of these structures are adjustable across the visible spectrum by changes in size. The sensitivity of the output wavelength on QD size translates into very precise manipulation of output color making them attractive components for use in light generating devices. Furthermore, emission spectra for QD based devices have been shown to be Gaussian in distribution – a departure from the non-symmetric energy distribution characteristic of organic materials. Indeed, OLEDs employing these particles as an emitting/electron transporting region with a polymer based hole transport layer have been examined by several groups.

Current trends in QD research have focused on core-shell type structures and in particular, those consisting of such II/VI semiconductors as CdSe<sup>24</sup>. These crystals are

formed using a synthetic method based on the pyrolysis of organometallic reagents, nucleation, growth, and annealing in a hot coordinating solvent - a procedure allowing for precise control of QD diameter and size distribution. Crystallites grown in this way are further characterized by a surface-capping region composed of a mixture of trioctyl phosphine and trioctyl phosphine oxide (TOP/TOPO). A wide variety of such organic capping layers exist but will not be mentioned in this text. This capped region acts to passivate the surface electronic states and results in greatly enhanced photoluminescence efficiencies. Photoluminescence quantum yield can be further improved with the addition of a second II/VI shell surrounding the core where typical materials used include CdS and ZnS. For this shell layer, an identical pyrolytic process is used but at a lower temperature to prevent further growth of the core material. The final structure is depicted in figure 3. Using the aforementioned fabrication techniques, QD samples may be generated with a size distribution of less than 6% standard deviation.



**Figure 3.** Structure of Shell-type Quantum Dot (Fig. From Ref. 17)

### 3.3 QD-LED Device Structure

Recent work at the Massachusetts Institute of Technology's Laboratory for Organic Optics and Electronics has shown that a QD light emitting device employing a small molecule host is indeed possible and functional<sup>25</sup>. A novel LED structure has been demonstrated that combines the ease of processability of organic materials with the narrow-band, efficient luminescence of colloidal QDs. A diagram of said device is shown in figure 4. As is apparent from the figure, the basic structure of this QD-LED is nearly identical to the hetero-junction OLED discussed earlier. What separates this device from

the OLED is the existence of a QD monolayer that acquires the role of emitting region from the Alq<sub>3</sub>. It is, in essence, a double-heterojunction device - holes injected into the TPD layer and electrons injected into the Alq<sub>3</sub> are transported to the QD region.

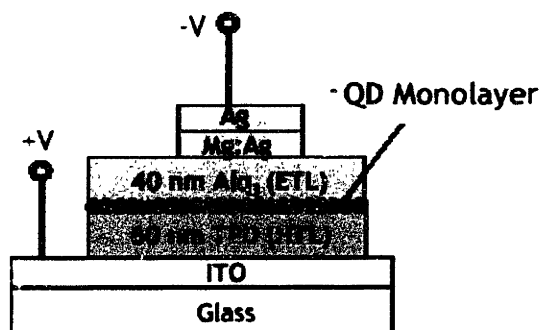


Figure 4. QD-OLED structure (Fig. From Ref. 17)

Excitons are then generated on the QDs in a parallel process combining direct charge injection and exciton transfer from organic host molecules. Light generated by recombination on QD sites results in tunable photon output between 540 and 635nm depending on QD size.

One of several breakthroughs realized in this new device was the formation of a self-assembled mono-layer of QDs, close packed and evenly dispersed over the surface of the hole transport layer. This is in contrast to earlier devices employing QD-multilayers roughly 10-20 layers thick. These early devices were characterized by a relatively low luminescence efficiency due to the dual function of the QD region as an emitter and electron transporter. In addition, these QD multi-layers suffered from a high density of pin-hole defects resulting in poor device consistency and performance. By employing a single monolayer structure whereby the emitting region is removed from the role of charge transport, these problems are avoided and subsequent device performance improved markedly.

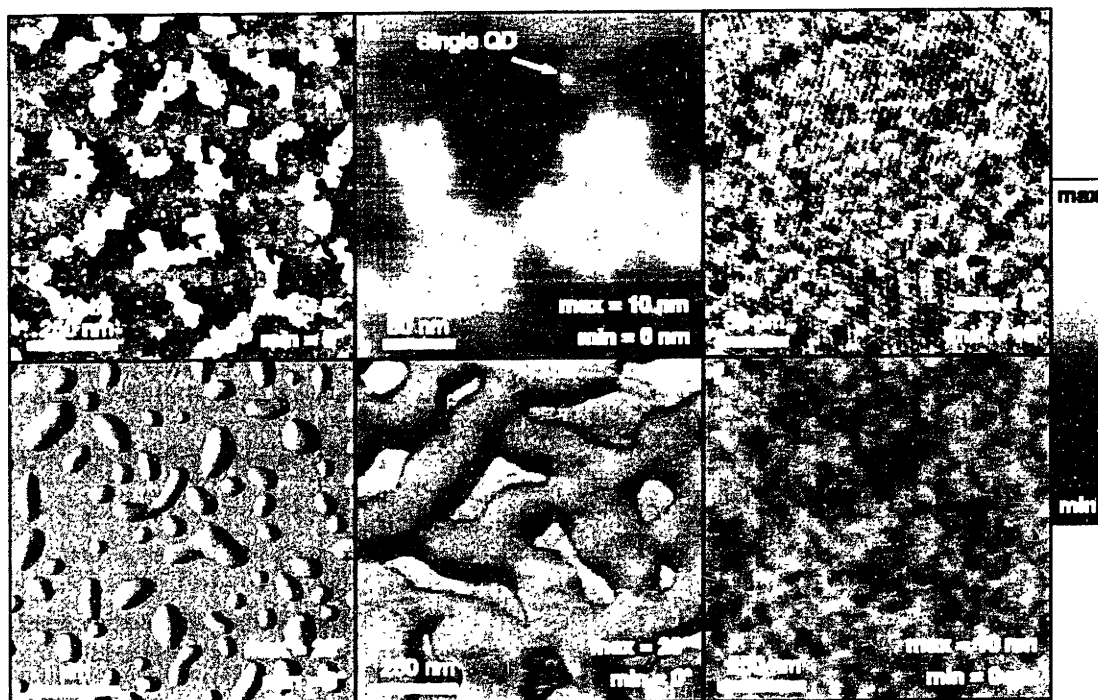


Figure 5 AFM images of various QD-OLED surface morphologies (Fig. From Ref. 25)

Formation of the TPD and QD monolayer was accomplished by using a novel phase-segregation technique in which a mixture of the two species, solvated in chloroform, was spin cast onto an ITO covered glass substrate. Effective phase-segregation is dependent upon the physical size of the two species involved along with their chemical nature. QD molecules are comparatively larger than TPD molecules and present a surface covered by TOPO/TOP chains as opposed to TPD, which is aromatic in character. This disparity results in the effective phase segregation of the two species. Phase segregation of the TPD/QD is dependant upon the spin on process in which both constituent species must be soluble in such solvents as toluene, alkanes and chloroforms. Furthermore, for efficient exciton transfer to occur from TPD to the QD layer, TPD emission spectra must sufficiently overlap with the absorption spectra of QD particles of all sizes. Both conditions are sufficiently satisfied by the TPD/QD mixture.

For efficient devices, it is crucial that the QD/TPD concentration be optimized for the formation of a single monolayer. Changes in the solution QD/TPD ratio may result in the formation of monolayer voids leading to contact exposure between TPD and Alq<sub>3</sub>. This results in larger emission fractions in Alq<sub>3</sub>, and thus poorer color saturation. Variations in coverage as a function of QD/TPD ratios during spin casting are shown in



Figure 5. Figure 5a depicts a phase segregated QD/TPD layer at 1/5 the optimal ratio. The resulting coverage in this layer is thus roughly 20% and is characterized by QD agglomeration. In contrast a fully optimized QD/TPD ratio spin casting is seen in figure 5c which depicts a close-packed uniform layer of QDs. Figure 5b shows a close-up of a QD island in figure 5a along with the associated length scale of a single QD.

### 3.4 QD-LED Device performance

Plot of intensity versus photon wavelength of a typical Alq<sub>3</sub>/TPD QD-LED and a similar device using an exciton/hole blocking 3-(4-biphenyl)-4-phenyl-5-t-butylphenyl-1,2,4-triazole (TAZ) layer are shown in figure 6. Emission spectra from the Alq<sub>3</sub>/TPD device show a sharp peak characteristic of the photoemission from QDs with core diameter of 38Å coated with 1.5 monolayers of ZnS. A second peak is observed corresponding to the broad emission from Alq<sub>3</sub> and is centered at roughly 530nm. In the second device, emission from Alq<sub>3</sub> is minimized through the use of the TAZ hole/exciton blocking layer which prevents either from being transported into the Alq<sub>3</sub>. The small peak corresponding to recombination in TPD is due to the small percentage of excitons that are generated deep inside this layer.

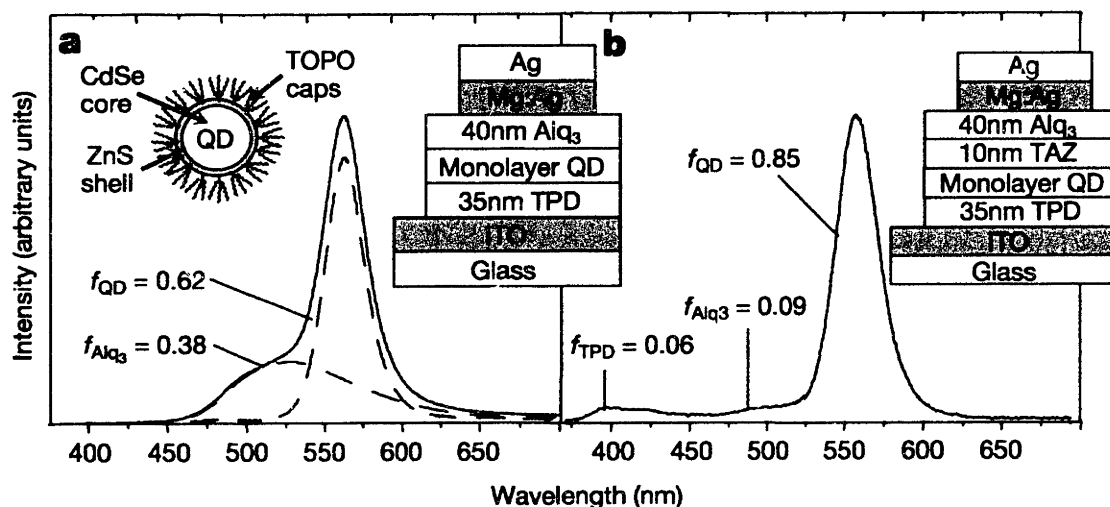


Figure 6. Emission Spectra for Devices I and II (Fig. From Ref. 25)

As depicted in figure 6a, the emission spectra of the QD layer is significantly narrower than for Alq<sub>3</sub> with full width at half maximum (FWHM) values near 30nm. This is due in part to the precise size control over QD fabrication (less than 6% standard

deviation) and also to the atomic structure of the CdSe QDs. Unlike organic molecules such as Alq3 whose large area, flexible structure contributes to broad emission characteristics, CdSe QDs are tightly bound, covalently bonded materials with fundamental FWHM values of 14nm (single QDs) at room temperature<sup>25</sup>.

A plot of the external quantum efficiency as a function of current density is shown in figure 7. For device 1,  $\eta_e$  exceeds 0.4% over a very wide luminance range with a peak value of 0.52% occurring at 10mA/cm<sup>2</sup>. Display screen brightness of 100cdm-2 is reached at 5.3mAcm-2. At 125mA/cm<sup>2</sup> a luminescence of 2000cd/m<sup>2</sup> is reached – values comparable to the best fluorescent OLEDs.

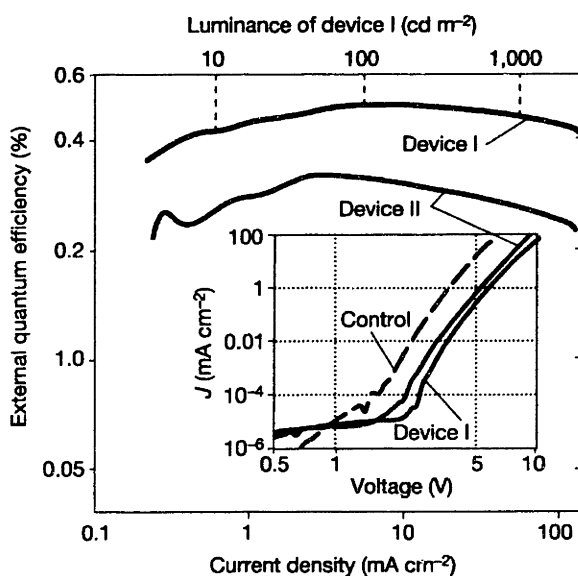


Figure 7. QD-OLED External Quantum Efficiency vs. Current Density (Fig. From Ref. 25)

### 3.5 Further Work

These recently announced results highlight the performance potential of QD-LED technology. The use of single monolayer active regions has resulted in devices with efficiencies 25 times greater than previous QD-LEDs. Such progress is a significant achievement considering the development history of the former. Yet even with these recent advances, a significant gap in performance remains when compared to current leading edge phosphorescent OLEDs with the demonstrated efficiency of such PHOLEDs orders of magnitude greater than that of QD-LED devices. Furthermore, issues have been identified in regards to the processing of QD-LED devices such as the 2-step

optimization process that is required in device fabrication. More specifically, one must first optimize the synthesis of the QDs in solution for a distinct emission spectra and then re-optimize the phase-segregation of these particles to match the output of the original dots. It would be much more efficient if one could limit the optimization process to a single step thereby limiting the complexity and uncertainty of QD-LED fabrication. Clearly, such a process will be required if production of these devices ever ensues.

Additional issues must be addressed as well before any commercialization attempts are made. For example, it is currently easier to fabricate QDs emitting at green wavelengths and higher than it is for emission in the blue; a result of the size correlation of QD output where smaller core diameters result in higher output wavelength. For deep, saturated blues, the control of diameter becomes significantly more difficult as QD cores shrink to the size of atoms. Decreases in dot size also lead to increased device inefficiency as the overall surface to volume ratio is altered to favor dangling surface bonds that may act as quenching sites. Finally, current solution processing techniques do not offer the precision needed for decent QD yield in this color range and therefore work must be done to further improve this process or develop new methods of QD formation.

QD failure modes and whether these might be similar to those of organic materials must be investigated as well. In particular, it will be crucial to understand whether or not QD lifetimes vary as a function of size. It is speculated that QD diameter will be an insignificant factor in degradation rate but this has yet to be confirmed. Collection of such data is not difficult and is just a matter of allotting time and resources to such a project. Additionally it must be determined whether or not exciton confinement on QD sites will contribute to increased lifetime as has been demonstrated for doped OLEDs. At this point, there is nothing that would lead against this idea, but this must still be proven using comparable lifetime data.

Another interesting question that has yet to be answered is in regards to the internal quantum efficiency of hybrid organic/inorganic LED systems. It has been observed that spin-singlet and spin-triplet mixing of exciton states occurs in QD based systems<sup>25</sup>. As discussed earlier in the context of phosphorescing OLEDs, such mixing of spin states followed by rapid recombination may lead to devices with 100% internal quantum

efficiency. The same results have not been obtained in QD-LEDs and further work is necessary to determine if such results are even possible.

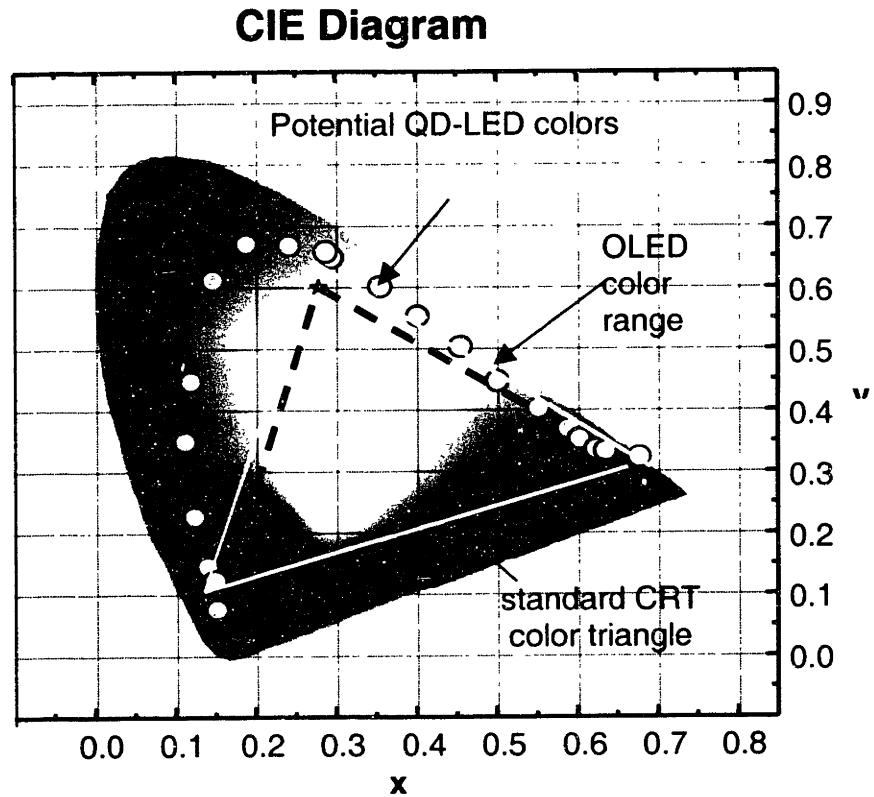
Irrespective of these issues, at this nascent stage of development QD-LEDs show large potential for use in flat panel display technologies. In further developing this device platform, researchers have discussed going away from the use of any organic layers thus distinguishing themselves from either the small molecule OLED or polymer LED developers – such is the reason for the lack of an “O” in the acronym QD-LED. The eventual goal of QD-LED investigators is the establishment of an independent device platform capable of competing, if not surpassing the two incumbent organic emissive technologies.

## **4.0 Applications**

### **4.1 QD-LED Applications**

Due to the embryonic nature of QD-LED research, gauging the potential of this technology within the growing OLED industry is a supremely difficult task. Indeed, even limited adoption seems very unlikely at this time. In recent discussions with Janice Mahon, the Vice President of Technology Development at Universal Display Corporation (UDC), it was noted that, “QD-LED research is too far in the horizon technologically for us to pursue as commercial product”<sup>26</sup>. A leader in the development of small-molecule based OLED devices, UDC holds non-exclusive licensing rights to the QD-LED device design for their partial funding of the research at MIT. Their view of QD-OLEDs is that of scientific curiosity, and have therefore focused their development efforts on the more mature areas of phosphorescent OLEDs (PH-OLEDs), flexible OLEDs, and organic vapor deposition systems - areas in which they are technological leaders. This sentiment appears to be felt by other key OLED developers as well, including Kodak and CDT with Kodak placing much of its research effort into small molecule fluorescent devices and CDT in polymer based devices. The only company remotely conducting any activity in this area is Philips Corp. who recently filed a patent for polymer-based OLEDs employing QDs as discrete emitters.

This situation could potentially bode well for an entity wanting to enter the OLED market or an existing group wanting to differentiate themselves from the current OLED technology path. As was alluded to in a prior section, the inherent attributes of QD-OLEDs may allow for products unattainable through traditional OLED materials - such as display screens with unprecedented color saturation. Because spectra for most cutting edge OLED dopants is broad, with average FWHM values around 60nm, there is significant loss of color to neighboring wavelengths. When used as RGB emitters in a display device, the combination of these color elements may result in a lower quality rendition of the desired image. Software algorithms could potentially alleviate such symptoms, but this would only serve as a band-aid to a problem easily solved using the narrower emission spectra of QDs.



**Figure 8.** CIE Diagram showing color gamut for QD-LEDs vs CRT (Source: MIT LOOE)

Additional limitations are presented in the generation of very deep, midnight blues - colors not possible using traditional OLED materials or any other RGB type displays, but

within the gamut of QD based devices. The CIE chart shown above compares the color gamut of CRTs to QD based devices and as is evident, the larger area encompassed by the QD points translates into a broader color gamut. These improved output characteristics of QD-OLEDs are a potential boon for graphic artists, video professionals, and high-end consumers who demand the highest standards from their display devices.

Additional applications may be realized as a result of the wide tunable range of solution processed QDs - a range which extends well into the near infrared. Current OLED materials are unable to emit in this region of the spectrum making QD-OLEDs the only alternative for developing infrared display devices. Such a device could prove useful in military applications by allowing soldiers to view information without the generation of visible light. With the combined use of standard military issue thermal goggles, this could be an effective way of relaying information for night operations where a visibly emitting display could potentially compromise the safety of the user. Such a display could combine the benefits of flexible OLED technology and be integrated into the uniforms of soldiers resulting in a compact, highly durable, and functional device.

In actuality, the benefits of QD-OLED technology may be implemented in all small-molecule based devices currently under development - from stacked (SOLED) and flexible OLEDs, (FOLED) to transparent OLEDs (TOLED) and polymer-based OLED structures. As the dots themselves are part of the device layer they may be easily incorporated into such devices without impacting their intrinsic properties. Furthermore, due to the size disparity between the average QD (nm range) and average LED device thickness, the impact on mechanical properties will be minimal. As such, it will be fruitful to conduct an examination of the current OLED display industry and view the potential applications of this technology.

## **4.2 OLED Display Industry Background**

Since the early work of Tang and VanSlyke, display technology has dominated the research and development focus for OLEDs and this will continue to be the case for the foreseeable future. The potential benefits of OLED technology are numerous and many view these advantages as serious disruptive elements to the more established LCD flap panel display (FPD) industry. Advantages that have been touted include increased

brightness and color resolution, wider viewing angles, lower power consumption, significantly greater form factor, and a potentially lower cost of manufacture. Adding fuel to the growing fire, early prototype displays have demonstrated excellent picture quality and performance exceeding similar sized LCD screens. As one industry analyst has stated<sup>27</sup>, there is an “aura of inevitability” associated with the success of OLED technology.

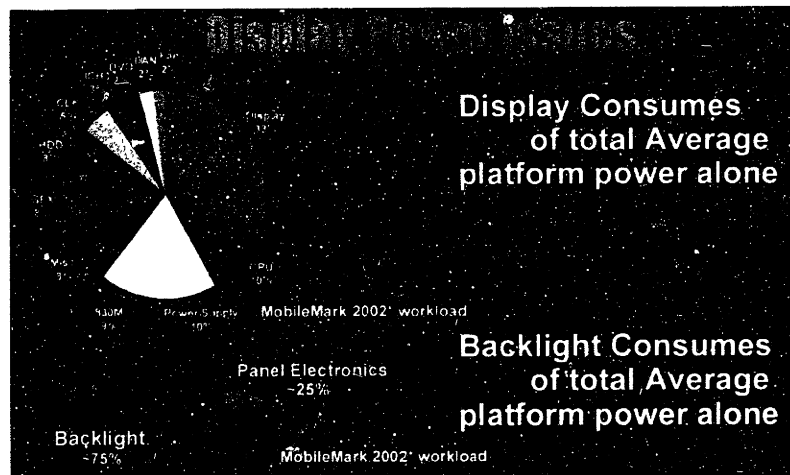
Yet, as with any emerging field, the OLED display technology is faced with a myriad of barriers, the most pressing of these being the inherent infancy of the industry itself. This fact has made bringing OLED based displays to market a monumentally difficult task, despite the successful demonstration of many promising prototypes. The infrastructure needed for such an industry to rapidly advance does not exist at this time and its development will be an evolutionary process as companies become more focused within the OLED value chain. Manufacturers are also struggling to develop efficient fabrication techniques and methodologies that will improve the low yields that are currently associated with these devices. Although beautifully simple structures when viewed individually, implementation of OLEDs into display systems with integrated backplane electronics is an exceptional challenge – one that brings along ever increasing problems and technological barriers. Companies involved in this endeavor are stepping into uncharted territory where the manufacturing knowledge base is small and the potential for innovation high.

Furthermore, incumbent Active-Matrix LCD (AM-LCD) technology has been fully embraced by major display makers and for this reason, OLED development may face additional delays. Driven by consumer demand for increased form factor and aesthetics, LCDs continue to advance at a rapid pace, making it difficult for other technologies to compete in the display marketplace. The LCD industry is characterized by mature and increasingly cost-efficient manufacturing techniques and extensive worldwide competition resulting in cheap, high performance display products. Furthermore, as the demand for such products show no indication of slowing down, major display makers are rightfully placing themselves in a position to squeeze the most that they possibly can from this technology. To further prevent cross-competition from OLED based displays, it has been suggested that major LCD manufacturers may not fully commit to the level of

development that they are capable of and that companies not traditionally associated with the display industry (ie. Pioneer and Seiko-Epson) will make the initial push<sup>28</sup>. Indeed, the first mass-produced, passive-matrix OLED display was released by Pioneer in 1999 as part of a car stereo system<sup>29</sup>. Since then they have sold over 7 million of these display units in both stereo and cell phone applications.

Current trends in the display market suggest that the isolation of OLED development to small, non-traditional players will be limited to lower-end technologies such as passive-matrix monochrome displays. Recently formed partnerships between display giant Sanyo Co. and Eastman Kodak (SK Display Corp.) along with activity from other display makers such as Samsung and Sony indicate the adoption of OLED technology by many of the major worldwide display makers for the development of more advanced active matrix color display systems<sup>30</sup>. Such widespread embracing of OLED technology further contributes to the inevitability of this technology. Display manufacturers are investing in OLED development for the long term while also investing in making current LCD technology more efficient and keeping LCD market share as long as possible.

As the global technology industry continues to develop, new windows of opportunity will open for OLED display makers to become major players. With the arrival of 2G and 3G wireless technology whereby video becomes the major form of communication, the necessity of cheap, high-resolution displays becomes a key product development factor.



**Figure 9.** Display Power Breakdown for LCD Display Systems (Source: Intel Corp.)



The same will become increasingly true for portable electronic devices from digital cameras and gaming systems to PDAs and laptop computers. For laptops in particular, display costs account for an increasingly greater portion of the total system cost as Moore's Law is not followed for optics. The list of materials required for LCD display manufacture are extensive, including glass and plastic substrates, photoresists, color filters, pigment dispersion materials for color filter, photomasks, sealing materials, spacers and liquid crystal materials. Furthermore, LCD systems require a backlighting source that not only adds to the total cost, but also consumes more power than all other laptop components (see figure 9). In contrast, material requirements for OLED displays are significantly smaller as a result of their self-emissivity. Total cost, although higher than comparable LCD displays, are expected to decrease to roughly 50-70% of a comparable LCD display as device yield improves and technology continues to mature<sup>31</sup>. OLED developers must keep to their promise of cheap manufacturing techniques and end products, as cost advantages will be as important as technical innovation in this field. Novel fabrication techniques from Roll-to-Roll processing and ink-jet printing of devices have been suggested and are key selling points for OLED based displays.

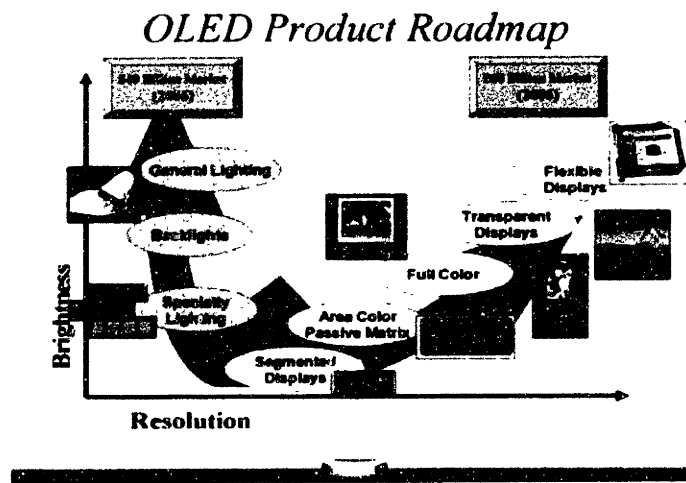


Figure 10. OLED Technology Roadmap (Source: Universal Display Corporation)

Figure 10 illustrates a general timeline for OLED products based on input from industry analysts<sup>32</sup>. As is evident, there is a diverging development scheme with one path focused on sub-component and area lighting markets and the other on display technology. For the latter, initial markets will be dominated by passive-matrix displays for small

devices like watches and portable electronics – similar to early stage development of LCD systems. This will be followed by emergence of full color AM-OLED screens primarily in personal electronics and later in larger display systems for PCs and television. Plastic displays will make their initial market penetration as replacements for glass based LCD systems, improving durability and significantly reducing weight. Fruition of flexible displays (the “Holy Grail” of the display industry<sup>33</sup>) is not projected until well after AM-OLEDs have reached the market and once transparent displays reach production. The delay will most likely prove beneficial for the flexible display industry as the technology is in need of a champion. Although not evident in the figure, it may very well be a while until OLEDs reach the profitability level of LCD technology.

The military applications arena, though not shown in figure 10, is one that will undoubtedly play a significant role in future OLED development. There is a growing interest in flexible displays within the armed forces due to potentially increased durability, lower package weight, and improved form factor<sup>32</sup>. Furthermore, the military is inserting greater numbers of FPDs into systems due to high visual content necessary for operation. eMagin, a company based in Hopewell Junction, New York, is currently working with the U.S. Airforce to develop a OLED based display for combat pilots. For pilots using night vision systems that amplify light from outside, it would be beneficial if information could be displayed as an overlay on that image and a clear OLED display would be perfectly suited for such an application. Other uses have been suggested including a helmet with a very bright microdisplay that superimposes an image that bounces off the visor towards the eyes. By looking at the image transmitted to the visor, the pilot can view what's ahead in the sky. The image must be bright enough so that even if the pilot is looking at bright clouds, the superimposed information shows what might be behind him.

In a similar fashion to the QD-based infrared display discussed earlier, a helmet or backpack with a swing-down display that provides the soldier with a map of the terrain, navigation information and real-time data on enemy positions has been discussed. The Army tested this concept with parachuting operations at night in unknown territory. Studies showed that reassembling and organizing troops averaged six hours. When the troops used a display connected to a global-positioning satellite system, that time was cut

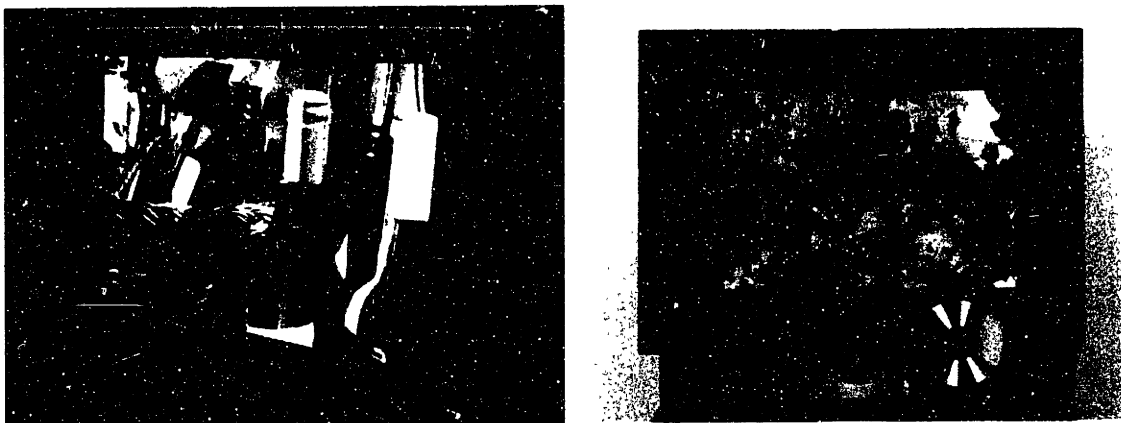
to less than an hour. Soldiers hitting the ground look at the display and find where they are and where they need to be. Such technology could greatly improve the efficiency of military operations and increase the safety of participating soldiers.

### 4.3 Current Performance

The state of OLED display technology is currently closer to the AM-OLED region in figure 10 than the PM-OLED area shown closer to the origin. Small-scale PM-OLED screens are in full production at this time by several manufacturers such as Pioneer and Seiko-Epson and are paced to becoming a commodity in the near future. AM-OLED fabs are currently in the ramping process as witnessed by the recent SK press release stating full production capability of their Gifu pilot line (Japan)<sup>34</sup>. They have announced the production of 2.16" AM-OLED displays with initial volumes of 100,000 units a month, ramping to over 1 million units/month by the end of 2003. Demand for these first production AM-OLED displays, which have 110,000 pixels and consume 270-300mW of power, is currently outpacing production capabilities, and the fact that display product manufacturers are requesting these units sooner than later is a testament to the arrival of this technology.

Based on Kodak and Dupont data<sup>16</sup>, OLED screens today have lifetimes around 10,000hrs or roughly 3.4 years of daily use (assuming 8 hours of use per day) – researchers at Kodak are trying to improve this number to 50,000hrs or about 16 years<sup>35</sup>. This is more than adequate for such personal electronics as cell phones where the turnover rate is on the order of year or more,<sup>36</sup> but will be insufficient for other applications such as portable electronics and large display screens. In the plastic display arena, UDC has demonstrated a video-rate, phosphorescent OLED display with 80dpi resolution, 120Hz refresh rate fabricated on 0.175mm polyethylene terephthalate (PET). The device is relatively small - 240x64 with a passive matrix drive scheme but is indicative of the tremendous commercial potential of flexible displays<sup>37</sup>. In what may be the most impressive OLED product to date, IDTech (a joint venture between IBM Japan and Chi Mei Corp of Taiwan) has announced the fabrication of a 20" AM-OLED display running at 1280x768 with a power consumption of 25W for 300cd/m<sup>2</sup>[7]. A comparable TFT display from Hitachi runs at 70W for 250cd/m<sup>2</sup>. Furthermore, they claim this

process is possible with existing LCD manufacturing equipment – meaning any current LCD maker may join in the OLED fray with lower than expected capital cost. Whether or not these claims are substantiated remains to be seen, but it does exhibit the rapid pace of OLED development. Displays from IDTech and Sony are shown in the figure below.



**Figure 11.** Sony 15-in and IDTech 20-in AM-OLED Displays (Source: Sony Corp. and Kodak Corp.)

#### **4.4 Competing Technologies**

There currently exist two opposing technologies within the OLED competitive landscape: small-molecule and polymer based devices. The field will remain this way for at least the foreseeable future unless additional device models such as QD-LEDs are able to emerge and establish themselves as independent entities. As was alluded to earlier, polymer based devices were discovered shortly after their small-molecule counterparts and since then, the development of each has progressed in parallel. Currently, both device designs command significant attention from research institutions worldwide with the most work in molecular organics conducted between Princeton and USC and polymer research led by Cambridge University. Differences in the physical and chemical structure of polymers lead to significant variations in fabrication and deposition techniques than those used for molecular organics. These differences must be examined carefully when considering the commercialization of either technology as they give rise to particular advantages and potential setbacks.

Polymers consist of relatively long chains of covalently bonded organic molecules giving them unique mechanical and electrical characteristics in the bulk<sup>38</sup>. They are easily

manipulated mechanically, as witnessed by the tremendous range of fabrication techniques from extrusion processes to moldability into complex shapes. Furthermore, recent advances in polymer electroluminescence have extended the usable range of these materials, allowing for novel light emitters and electrical structures. Polymers conduct by a mechanism in which overlap of the double bond p<sub>z</sub>-orbitals forms a system of delocalized  $\pi$  electrons. Bonding and anti-bonding orbitals form the equivalent of conduction and valence bands respectively, allowing efficient carrier motion along the axis of the polymer chain. The resulting carrier mobility in common polymer substances such as PVK are high with values near 0.2cm<sup>2</sup>/Vs. The nature of the polymer backbone facilitates the addition of functional side groups, thereby tuning the emission characteristics of the material. Electron donating groups shift the emission to lower energy while electron-accepting groups shift the emission to smaller wavelengths with the span covering most of the visible spectrum. Conductivity may be further tailored in polymers by doping to effectively shift their electrical classification from semiconductors to conductors. Some commonly used polymer structures are shown in the figure below

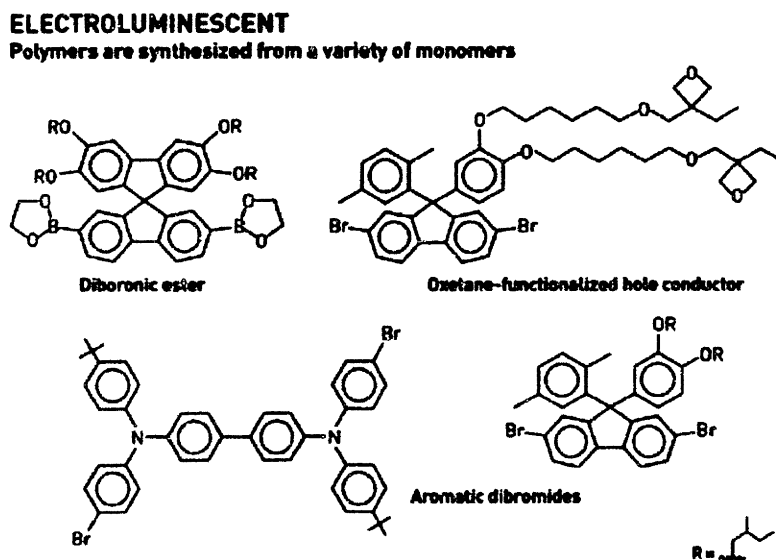


Figure 12. Common Electroluminescent Polymers (Source: Chemical and Engineering News)

Unlike molecular organic structures, whereby organic layers are deposited using thermal evaporation in a vacuum, polymer layers are formed by spin or dip coating the

underlying substrate. For the spin on process, the substrate is placed in a rotating chuck and a small amount of solvated polymer material applied to the center of the rotating substrate. Centripetal forces spread the applied solution across the substrate whereby surface tension and adhesion result in uniform coverage. Subsequent baking evaporates the solvent leaving behind a polymer film. Care must be taken in maintaining an impurity free ambient during the spin-on process as any foreign substance may drastically reduce the conductivity of the final device and increase the quenching rate of excited states. Spin-on processes give rise to additional issues when fabricating multiple layer devices such as heterojunction structures. The solvent used in the second and subsequent layers must not dissolve the polymer layer(s) below making chemical compatibility a key issue in device fabrication.

These fundamental issues have led PLED developers to other processing routes, the most promising of these being ink-jet printing and masked dye-diffusion. In the ink-jet process, the ink cartridge of a standard printer is replaced with a similar container holding the polymer/solvent solution. The solution is then fed into a series of nozzles, whereby polymer droplets are jettisoned onto the substrate in a controlled and precise manner. A potentially fast, low cost printing method over organic substrates, ink-jet development is a significant selling point of OLED technology today. Applications for this technology are not limited to the fabrication of the light-emitting layer but may be used in printing the supporting thin film transistor array as well. Companies such as Xerox PARC have demonstrated 20um minimum feature size (determined by drop size) and layer registration on discrete and self-aligned TFTs in a matrix addressing structure<sup>39</sup>. Many believe the combined ability to deposit the backplane electronics with the emitting layers will be a crucial development tool for future flexible display systems.

Masked dye diffusion is a process in which dopants may be driven into a large area polymer substrate in a single step making this technique faster than ink-jets for certain applications. In this process, an intermediate mask is placed between the dopant source and the polymer substrate. Once heated, dopant diffusion occurs resulting in the patterning of active, light-emitting regions on the substrate. There have been demonstrations in literature where red and green dopants were introduced in a blue

emitting PVK material (71.5% by weight) resulting in substrates with all three pixel colors.

The advantages of polymer based OLEDs are primarily focused on the manufacturing processes involved and thus are a bit theoretical at this point. Polymer developers state that unlike small molecule devices, PLEDs may be fabricated under atmospheric pressure and room temperature. This negates the need for expensive vacuum equipment and thus drastically cuts manufacturing cost and cycle time. These benefits further allow PLEDs to be fabricated on large substrates, a difficult task if high vacuum is needed. The use of polymer ink-jet printing for the combined fabrication of the TFT backplane and the overlying light-emitting layer is currently the only proposed option for such a dual-stage process.

Due to strong exciton-phonon coupling in polymer chains, the emission spectra of pLEDs is characteristically broad with spectral widths near 100nm. Narrow, saturated colors are difficult to obtain due to further dispersion in conjugated lengths. Furthermore, the benefits of low cost spin-on processes may not be the champion once thought to be as the only method currently available for depositing and patterning the top electrode is through a vacuum evaporation process. Additional questions have been raised regarding the quality and device yield possible with non-vacuum systems as initial quality has not met expectations. Clearly, as with small-molecule systems, a significant amount of development work remains for PLED devices.

#### **4.5 Dendrimer Based PLEDs**

Light emitting dendrimers constitute a new but rapidly maturing materials technology for PLED systems, one that has gained significant interest from major technology developer CDT<sup>40</sup>. Dendrimers comprise an organic or organometallic light-emitting core, which is connected to surface groups by branched organic dendrons<sup>41</sup>. The dendritic structure controls core-core interactions and hence the photoluminescence and device properties of the materials. The characteristics of these emitting elements are very similar to those of semiconductor QD emitters such as being solution processable and capable of tuned light emission. One of the key advantages of this structure is that core material can be chosen from select phosphorescing metallic elements whilst the surface groups can be selected to give the desired solubility. This results in a structure capable of

incorporating both singlet and triplet emission, much like the small molecule phosphorescents discussed earlier, with internal quantum efficiencies reaching a theoretical value of 100%. A second advantage is that quenching of luminescent excitons is also reduced as a result of the distance between the core and the branching dendrons.

Dendrimer technology has already produced sizeable results, as witnessed by recently reported high-efficiency green OLEDs with 40lm/W luminescent efficiency at 400cd/m<sup>2</sup> and 4.5V<sup>42</sup>. Turn-on voltages were normally 3.0 V and a maximum brightness of 12000 cd/m<sup>2</sup> at 7.0 V has been observed. Such results make these devices some of the most efficient OLEDs ever and build on a previous announcement of 6.9lm/W at 1500cd/m<sup>2</sup>. Dendrimer technology may prove to be the medium by which PLEDs will advance to meet the performance of small molecule devices. Rival CDT, further proving the potential of this technology, has recently bought out the principle developer of this technology, Opsy Display Systems. Continued research is required, but the early acceptance by a major PLED developer has made dendrimers appear promising as a technology solution.

## **5.0 Intellectual Property**

This section presents a brief overview of patents relevant to the field of QD-OLEDs and is limited to those that may play a role in the future commercialization of this technology. The patent search was conducted using the United States Patent and Trademark Office (USPTO) database and thus focus has been placed on patents filed or submitted in the United States only. This search is by no means a complete listing of patents that may hold relevance - the intention of this section is to highlight key aspects of the intellectual property field and to identify those patents that may hold blocking potential for a QD-OLED venture. To this end, focus has been placed on analyzing patent claims covering QD and QD-LED related technology.

The field of relevant patents may be broken down into three main groups: patents specifically addressing QDs and QD-LED technology, materials technology for OLED applications, and OLED processing methodologies. As the incorporation of QD structures in organic light emitters is still a technology in its infancy, very little IP currently exists in



this area with a majority of key patents held by academic institutions rather than industry. Materials technology covers those patents dealing with the development of novel material systems such as hole and electron transport materials, high efficiency emitting materials and dopants, materials for electrical contacts, and barrier technology. Eastman-Kodak, UDC and Cambridge Display Technologies (CDT) currently have the broadest portfolios in this segment while Vitex Inc. is a key holder of encapsulation and barrier material IP. Processing methodology covers patents discussing deposition and fabrication technology such as organic vapor phase deposition and ink-jet printing. UDC in partnership with Aixtron and several key display manufacturers such as Samsung SDI and Sanyo hold the primary patents in this field. All relevant patents that have been listed in the following sections have been issued within the past decade, well within the standard lifetime of 20 years.

### **5.1 QD and QD-LED Related Patents**

For their research in quantum-dot based light emitting devices using small-molecule organic hosts, the MIT group (Bulovic et al.) have recently submitted applications for two patents – one describing the basic structure of a QD-LED device (“Efficient QD-LEDs Using Organic Host Materials”, MIT case number 9924) and the other detailing the phase segregation technique used in creating the QD monolayer (“A Method for Generating Thin-Film Multilayers by use of Material Phase Segregation”, MIT case number 9562). Both patents are still in the application phase and require processing by the institution before submission to the USPTO. Although analysis of claims was not possible at this time due to the state of the application, general details may be inferred from the data and results that were discussed earlier. It may be said without question that both applications will be fundamental components of an IP portfolio for a startup company involved with QD-LEDs.

Additional patents relevant to the QD arena are primarily involved with the synthesis of the QD structures themselves. Most notable among these is patent 6,207,229, submitted by Bawendi *et al* which describes the fabrication of coated nanocrystals capable of light emission. As stated in the claims, these structures are composed of a substantially monodisperse core material selected from a group of II-VI semiconductors

surrounded by a second layer selected from an another II-VI group. Core material is chosen from the group consisting of CdSe, CdTe, CdS and mixtures while the second is taken from the group consisting of ZnS, ZnSe, CdS, CdSe and mixtures. These nanocrystal structures are characterized by a core diameter ranging between 25 and 125 Å and by a spectral range of emission no greater than 60nm. Further, they must exhibit quantum conversion efficiencies of greater than 30% and have core diameter variance of no greater than 10%(rms). The primary claim describes a fabrication process in which the core semiconducting material is solvated with a thermally convertible precursor used to form the second semiconducting layer. As stated in the invention summary, “The coordinating solvent is maintained at a temperature sufficient to convert the precursor into the second semiconductor material yet insufficient to substantially alter the monodispersity of the first semiconducting nanocrystal.” The layered nanocrystallites are further exposed to an organic compound having an affinity for the nanocrystal surface and that displaces the coordinating solvent. This leads to the formation of an organic cap matrix which acts to passivate the nanocrystal and improve its spectral properties. The final product is the formation of a quantum-dot shown in figure3 – a functional light emitting device composed of three primary components. The aforementioned processes describe, in general, the techniques used for the fabrication of QDs in the experimental devices.

Other patents for the fabrication of QD structures have been filed, including patent number 6,225,198, submitted by Alivisatos et al entitled, “Process for forming shaped group II-VI semiconductor nanocrystals, and product formed using process.” This patent describes a fabrication process where group II and VI precursors, suspended in a binary solution of phosphorous-based surfactants, form nanocrystalline structures whose shape may be controlled by the ratio of the involved surfactants. The resulting nanocrystals have been shown to vary in shape – larger concentrations of the first surfactant will promote the growth of spherical dots while the reverse will result in more tube-like structures. Clearly this method is substantially different than one above and thus brings to light the nondescript nature of QD fabrication - nuances in method abound for techniques that have been defined above. The blocking potential for any such patent discussing the

fabrication of QDs is thus extremely low and may effectively be disregarded for commercial applications.

Patents discussing OLED devices utilizing QDs as active emitters have been filed but are primarily limited to those employing non-molecular organic materials. Patent number 6,501,091 entitled, "Quantum dot white and colored light emitting diodes," claims a device in which nanocrystals, identical those described by patent 6,207,229, are dispersed in a host matrix composed of polystyrene, polyimides, epoxies, silica gels, or silica glasses. The device is further defined as having a separate light source - resulting in the emission of light both by the source itself and by the QDs whose output is dependent upon physical diameter. Patent number 5,537,000 entitled, "Electroluminescent devices formed using semiconductor nanocrystals as an electron transport media and method of making such electroluminescent devices," describes a device more similar to the QD-LED structure in question. The patent lays claim to any number of electroluminescent devices characterized by 1) a hole injection and transporting means 2) electron transport means in contact with said hole processing means comprising one or more monolayers of semiconductor nanocrystals 3) electron injecting means in contact with said electron transport means 4) where said semiconductor nanocrystals comprise group II-VI semiconductors 5) where said semiconductor nanocrystals comprise group III-IV semiconductors 6) wherein said electron transport means comprises a plurality of layers of said semiconductor nanocrystals. Subsequent claims set forth in this patent are extremely broad and even goes as far as listing specific display devices employing II-VI nanoparticle emitters as covered items. However, one of the underlying requirements in all listed claims is the necessary condition that the hole transport medium be in direct contact with the electron transport medium. Because the QD-LED design in question uses a QD monolayer as a discrete emissive region, isolating them from charge conduction duties, the claims in this patent are fully inconsequential. There is no mention of using a distinct emitting region physically separated from the electron and hole transport materials. Other patents such as 5,751,018 which discuss the formation of nanocrystalline monolayers on inorganic surfaces are too specific in that they are limited to a certain class of substrates. If further development of QD-LED structure leads to the removal of

organic layers and the subsequent use of materials listed in this patent, it may then become a potentially blocking entity.

At this time, only one patent has been identified as having the potential to block a QD-LED venture. The document in question is currently in the application stage and was submitted by researchers at the Philips Corp. in the Netherlands. It is listed as patent application 01121146.3 and titled “Electroluminescent Device Comprising Quantum Dots”. The primary claim describes a device with the following requirements: *1) An electroluminescent device comprising: a) hole processing means (2) capable of injecting and transporting holes; b) a light emitting layer (3) in contact with said hole processing means (2), comprising quantum dots; each of said quantum dots being provided with at least one capping molecule with functional unit on the quantum dot surface which causes excited state injection into the quantum dot; and c) electron processing means (4) in contact with said light emitting layer (3) for injecting and transporting electrons into said light emitting layer (3).* The patent further lays claim to various chemical species and material types that may be used as hole and electron transporting means and for materials used as QD capping layers. Although broad, the blocking potential appears to be diminished by the statement given in (2). The description of the capping molecule as a functional unit promoting injection into the QD is contrary to the function of surface entities of recent QD-LEDs. For the latter, organic surface states serve only as a buffer region and do not participate in the transfer of excited states into the core<sup>43</sup>.

## **5.2 Materials Technology Patents**

Understanding of the patent field pertaining to OLED material technology will be crucial for any venture seeking to develop useful devices and in particular, those devices employing QDs. Primary patents in this field pertain to the use and manufacture of materials as hole and electron injecting means, hole and electron transport means, and light emitting means either by doping or in conjunction with said transport means. Early hole transport materials including the group of phthalocyanines (such as the commonly used CuPc), porphyrinic compounds, and various diamine and aromatic tertiary amines are claimed in patent numbers 4,356,429, 3,935,031, and 4,769,292 respectively. Patent 4,769,292, further lays claim to several electron transport materials such as tris(8-

hydroxyquinolate)aluminum along with the first mentioning of the use of a fluorescing dopant. Electron transport materials are further listed in pat. 5,925,472, especially those in the metal chelate category. Such patents may be potentially blocking if the device structure of figure 3 is used which employs separate organic hole and electron transport materials. As noted earlier, further development of QD-LED devices devoid of any organic host materials will, for certain, negate the blocking potential of many OLED material patents.

### **5.3 OLED Processing Patents**

Intellectual property in the area of OLED deposition and fabrication technology is broad, but the pertinence of such technology to the development of QD devices is currently limited. Most of the required knowledge in small-molecule OLED production is in high vacuum, thin film evaporation technology – an area that has been in public domain for quite some time. However, patents do currently exist in the area of Organic Vapor Phase Deposition (OVPD) and must be given attention to if a QD-LED venture is to create and market a deposition system. For a startup involved solely in the licensing of QD-LED technology, this will not pose a problem

## **6.0 Business Analysis**

### **6.1 Business Model**

Although QD-LEDs have been in existence for several years, their commercial potential has never been realized due to the low external quantum efficiency of early devices. Successive improvements by Bawendi et al<sup>23</sup> and later on by Alavisatos et al<sup>24</sup> were key in raising the performance bar, but the efficiencies of the best devices were still orders of magnitude lower than the best all-organic OLEDs. Only recently, with the demonstration of a vastly more efficient device using a novel organic/inorganic hybrid structure, has the thought of commercial entry for QD-LEDs been addressed. Indeed, the MIT researchers responsible for recent breakthroughs have made it clear that display product realization is a primary driving force for continued research<sup>44</sup>. This fact in mind, it will be a fruitful endeavor to examine some of the basic factors and issues pertaining to

a QD-LED venture. In this section, a basic business structure will be outlined describing key goals and strategy for a QD-LED startup. A comprehensive business plan and cost model analysis is beyond the scope of this paper.

In developing a business strategy for a QD-LED venture one must assess the aims and capabilities of the initial business venture and to then apply a business model that will best meet the needs of the startup. It may be beneficial to adapt the corporate model of a small, recently formed business and to this end, several potential companies come to mind. The most promising of these appear to be UDC and Nanosys Inc. – both companies are fairly new with UDC established in 1994 and more recently, Nanosys Inc. in 2001. UDC has established a three-pronged corporate strategy based upon their exclusive right to license technology from partners Princeton University and USC. Their strategy is made up of the following components: 1) Funding research and development of OLED technology with its primary research partners and other institutions 2) Development of reliable product and process technologies and 3) Licensing the technology and entering into joint ventures and other strategic partnerships with experienced manufacturers, suppliers of display products, materials and equipment manufacturers and material developers. In a similar manner, Nanosys Inc. has also stated its primary strategy as being the development of several nanotechnology programs through aggressive technology in-licensing, and internal development. Their commercialization scheme is similarly based upon the formation of strategic partnerships with interested companies. However, in contrast to UDC, Nanosys incorporates manufacturing capabilities into its agreements by supplying “nano-enabled” modules, allowing partners to integrate Nanosys’ technology seamlessly into their own existing products. The success of both companies lies, in part, to the successful development of their core competencies.

Due to the state of QD-LED technology and the limited resources available in early stages of business, it will be most appropriate to model the startup along the lines of UDC– that of a technology development and licensing body. As with UDC, manufacturing capability will be foregone with focus rather placed on the development of core technology. Development of products for market will be left to targeted licensees who have the resources to conduct such activities. As such, a list of mission goals have been summarized in the following:

- As primary goal, develop fundamental device and manufacturing technology for QD-LED products
- Generate key intellectual property in the field of QD-LEDs and acquire relevant IP from other developers in the field
- Actively pursue licensing agreements with leading OLED display and components manufacturers.
- Develop QD-LED technology as a competitive display platform against both small molecule OLED and polymer LED technologies

In following such a corporate strategy, it will be crucial for the technology to be developed to the extent that it will meet and even outperform current competition in a short period of time. Licensing efforts must also be aggressive as there are several companies now that are attempting or have already entered the market in this way. Most importantly, however, will be in developing partnerships with such QD makers as Nanosys Inc. and Quantum Dot Corp as efficient and cost effective methods for QD fabrication must be demonstrated long before licensing efforts even take place. Due to the limited size of the QD market, volume production of QDs is currently not possible and will not be for the foreseeable future. Furthermore, attempts to establish a self-sustaining QD manufacturing capability will be more detrimental to overall productivity and profitability in the initial stages of business. Development of a large-scale production equipment, possibly similar to the continuous flow system used in Professor Bawendi's lab at MIT, will be crucial for the future of QD based devices. Collaboration must further address the issues and the additional work that was mentioned in an earlier section.

Even then, long-term profitability may be difficult to accomplish. Once the OLED market becomes more mature, it may be a challenge for small, technology developers to compete with larger companies like Kodak that are more diversified in the value chain. In grim reality, the existence of these small, technology developers will be in the hands of the larger manufacturers as 1) there is always the chance that such large companies will develop technology surpassing that of the independent developers and 2) because smaller corporations will not have the resources and means to establish large scale manufacturing

capability to attain self-reliance. In an ideal venture situation, once QD-LED technology is developed to the extent that it becomes a significantly differentiated and marketable technology, a larger manufacturer will acquire the technology, along with the core business. There are too many variables in the current market for a clear and accurate strategy to be developed and only time and changing demands will determine the correct commercialization path.

## **6.2 Extended Business Plan**

A business plan has been devised that will cover the development path for a QD-LED startup in the first five to six years of existence and is characterized by three stages: 1)an early technical stage 2)a second technical stage and 3)an execution stage. The early technical stage is usually focused on demonstrating proof of principle. With the recent exhibition of working QD-LEDs based on hybrid organic/inorganic materials – this task has already been accomplished by researchers at MIT. The NSF-MRSEC programme, DMR, and Universal Display Corporation were the principle financiers for this preliminary work. Additional tasks during this initial phase will involve working with MIT's Technology Licensing Office in obtaining exclusive rights to the two fundamental QD-LED patents discussed earlier. Talks with QD makers and venture capitalists must also be pursued to begin formation of technology partnerships and to acquire funding for the second stage respectively. An estimated cost of \$600,000 incurred during this phase will be covered by early round VC seed funding and will consist of legal fees associated with patent licensing/advice along with travel expenses. Duration of this initial stage is expected to last no more than one year.

Having demonstrated principle, funding for the second technical stage must be acquired for further technology and business development. An estimated \$3 million dollars will be needed in this round to acquire building facilities, an employee base of 4 scientists, 2 office personnel and 2 business developers, a deposition systems with attached hood, data analysis equipment, lab hardware, and office equipment. Funds will also go towards legal fees and the high cost associated with device materials. Financial support will be sought through venture capital and through government contracts from DARPA and the DoD. Activities during this phase will consist of three primary tasks 1)



Continued scientific research to address the issues outlined in section 2.5 and to develop a QD-LED patent portfolio 2) establish partnership(s) with QD suppliers and developers and 3) actively begin pursuing licensing agreements with potential customers. Reaching important milestones such as the demonstration of quality devices spanning the theoretical emission range of QDs will be needed to obtain further funding in successive rounds. The second round is anticipated to take up to two years.

The execution stage will span the next two to three years, and during this time technical focus will be placed on developing efficient manufacturing techniques with QD suppliers and in investigating other potential routes for QD-LED commercialization. An additional \$8-10 million will be required at this stage to support expanding business needs and the growth of the work force to include additional scientists, technicians, computer specialists, and business people. It is expected that revenue from licensing agreements will be well underway at this stage, with additional funding coming from cost sharing with technology partners and established government contracts. It may be beneficial at this point to begin expanding into QD fabrication and development through technology cross-licensing and by bringing acquiring a team of capable chemists. Doing so will decrease our financial liability to QD developers which is expected to be high.

An examination of a developing startup like UDC, which targets partnerships and licensing of technology as primary sources of revenue, reveals the large financial uncertainty that is characterized by such a business model. UDC has not posted a single profitable quarter between 1997 and 2001, with net losses in 2001 amounting to \$18,873,436. Furthermore, the company has anticipated continued losses for the foreseeable future. Although successful in leveraging their primary technologies, in the end the success of UDC will be in the hands of display manufacturers as they control whether such technology will be adopted or developed on their own. These facts highlight the difficulties faced by independent technology developers in the OLED industry and the importance of forming strong partnerships with larger corporations. For a QD-LED startup attempting to establish the technology as an independent platform, the adoption of the technology by key manufacturers will be essential for future success.

### 6.3 OLED Market Performance

The potential return for a successful venture in the OLED display industry is high. As shown in figure 13, growth rates for the FPD industry have been impressive despite adverse economic conditions worldwide. According to industry consultants at DisplaySearch, growth rates for the FPD industry in 2002 were estimated at 47%, growing from \$22 billion in 2001 to \$32.3 billion in 2002<sup>27</sup>. Among the various display technologies, OLEDs have demonstrated the highest growth rate over the past several years. Nonexistent before 1999, the OLED market has since then taken off, with expected growth rates reaching 200% for 2003 (measured by percentage change over previous year) as seen in figure 14 below. This value is expected to increase over subsequent years with industry experts projecting 56% CAGR between 2002 and 2009 (figure 13). Indeed, OLED market value has been valued at \$91 million in 2002 and projected to grow to \$1.2 billion by 2006. Depending upon the acceptance of early product offerings, this may be a conservative estimate according to several manufacturers.

Oct. FPD Price Survey: New Lows in Street Prices Bode Well for Demand October 15, 2002

Exhibit 21. FPD Market Revenue Model, by Technology Type

	1996	1997	1998	1999	2000	2001	2002E	2003E
<b>Passive Matrix LCDs</b>	3,590	3,600	3,209	3,907	5,358	5,324	3,600	3,400
% Y/Y	NA	0.3%	-10.9%	21.8%	37.1%	-0.6%	-32.4%	-5.6%
<b>Thin Film Transistor (TFT)-LCDs</b>								
<i>of which:</i>								
a-Si TFT-LCDs	5,409	6,022	6,241	13,088	16,385	13,975	20,300	25,100
% Y/Y	NA	11.3%	3.6%	109.7%	25.2%	-14.7%	46.3%	23.6%
LTPS TFT-LCDs	111	124	128	303	441	505	600	1,100
% Y/Y	NA	11.3%	3.6%	138.4%	46.4%	14.6%	18.7%	83.3%
HTPS TFT-LCDs	390	434	450	483	571	581	600	600
% Y/Y	NA	11.3%	3.8%	7.3%	18.2%	1.8%	3.3%	0.0%
<b>Total TFT LCD</b>	5,910	6,580	6,819	13,874	17,397	15,061	21,500	26,800
% Y/Y	NA	11.3%	3.6%	103.6%	25.4%	-13.4%	42.8%	24.7%
<b>Plasma Display Panels (PDPs)</b>	50	160	266	340	561	1,226	2,000	3,000
% Y/Y	NA	220.0%	66.9%	27.6%	65.2%	118.4%	63.1%	50.0%
<b>Organic Light Emitting Diodes (OLEDs)</b>	0	0	0	15	21	51	100	300
% Y/Y	NM	NM	NM	NM	37.4%	145.9%	95.9%	200.0%
<b>Others</b>	865	862	708	842	1,023	1,180	1,400	1,500
% Y/Y	NA	-0.3%	-17.9%	18.0%	21.6%	15.3%	11.4%	6.9%
<b>TOTAL FPD REVENUES</b>	10,215	11,202	11,003	18,578	24,341	22,541	28,500	35,000
% Y/Y	NA	10.0%	-1.8%	72.6%	26.0%	-8.2%	30.2%	22.1%
<b>TOTAL FPD CAP-EX</b>	2,075	2,087	2,000	4,271	5,448	6,298	8,500	9,707
% Y/Y	NA	0.6%	-4.2%	112.9%	21.8%	15.3%	33.8%	14.3%
<b>CAP-EX/REVENUES</b>	19.8%	18.7%	17.7%	22.9%	22.4%	27.9%	29.8%	27.7%

Source: CIBC World Markets Estimates, DisplaySearch, IDC

Figure 13. Market breakdown of FPD industry (Source: CIBC World Market Estimates, DisplaySearch)

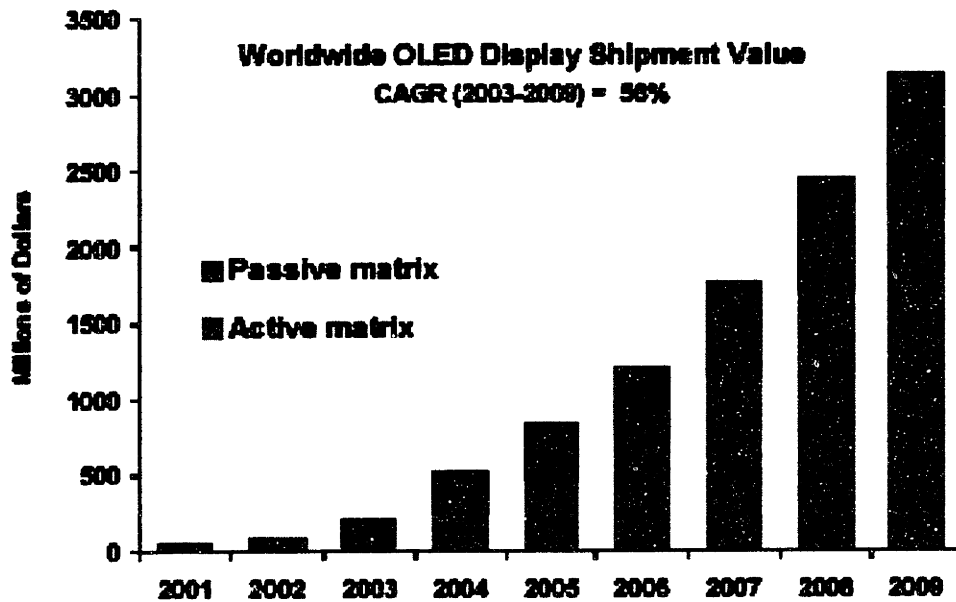


Figure 14. Worldwide OLED Shipment value (Source: iSupli/Stanford Resources, 2003)

## 7.0 Conclusion

Recent demonstrations of a light-emitting device employing a self-assembled monolayer of semiconducting quantum dots has ushered a potentially new design paradigm for the OLED industry – the QD-LED. Unlike incumbent technology, which is characterized by molecular or polymeric emitters, QD-LEDs utilize inorganic nanocrystals that are tunable across the visible spectrum. Narrow-band emission has been observed for QD-LED devices, with demonstrated FWHM values of 32nm and external quantum efficiencies of 0.4% - a 25-fold improvement over previous devices using QD emitters. These attributes have opened up opportunities for QD-LEDs not possible with other technologies with potential applications including displays with greater color saturation and displays capable of emitting in the infrared. More importantly, QD-LEDs may eventually exist as an independent platform in today's OLED display industry – a

boon for companies wishing to enter the market and a potentially lucrative source of licensing revenue. For display manufacturers adopting this technology, the versatility and tunability of quantum dots may allow for decreased materials cost in both development and storage, while potentially offering efficiencies similar to phosphorescent based systems. Furthermore, QD based displays may alleviate several of the problems associated with molecular and polymer based OLEDs such as differential color lifetime and overall degradation rate.

With the timing of recent QD-LED announcements, companies or institutions pursuing this technology are few, if not nonexistent. Examination of the related patent field has also revealed the lack of blocking intellectual property, easing the legal barriers for a QD-LED startup. The window of opportunity for such a venture thus appears wide, but as outlined in an earlier section, several key hurdles remain before a QD-LED business may reach a working stage. Advancing the technology to a point of comparable efficiency with the best fluorescent and phosphorescent devices will be a major challenge. Furthermore, substantial work lies in creating an efficient manufacturing process for QD based devices, as the current QD industry cannot support large-scale production.

History has seen many once promising technologies come and go – a trend not indicative of current OLED technology. Rapid expansion of the industry and its early adoption by both established companies and newcomers, are strong indications of its continued success. With continued research and demonstration of improved performance, QD-LED technology may penetrate the growing OLED market and establish itself as an independent platform. This will serve only to benefit the industry through the infusing of new ideas and subsequent broadening of the competitive landscape.

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