

# Organic Light Emitting Devices From Displays to Lighting

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Recently there has been significant interest in electroluminescence from organic materials. Driven by the potential to significantly impact the information display market, research and development on organic light emitting devices has advanced at a remarkable pace over the past decade or so.<sup>1,2</sup> Here we present the basic ideas governing the operation of organic light emitting devices (OLEDs), highlight areas of progress, and discuss emerging applications in displays and future applications in lighting.

An organic light emitting device consists of one or more semiconducting organic thin films sandwiched between two electrodes—one of which must be transparent. A simplified schematic of a typical OLED is shown in Fig. 1. Indium tin oxide (ITO) is utilized as the transparent anode electrode and an evaporated metal is utilized as the cathode. The device is fabricated by sequentially depositing the organic thin films followed by a shadow mask defined thin metal cathode onto a transparent substrate such as glass or a flexible plastic. When a forward bias is applied, injected electrons and holes recombine in the organic layers to generate light. Also shown in Fig. 1 are representative materials from the two major classes of organic semiconductors used in fabricating OLEDs: low molecular weight materials (small molecules) and higher molecular weight materials (polymers). Efficient electroluminescence (EL) from organic materials was first reported in 1987 by a team of researchers at Kodak.<sup>3</sup> Previous work on organic EL using thick single crystals was deemed impractical due to high voltages and low EL efficiencies. However, the Kodak report demonstrated that thermally evaporated, amorphous thin films of small molecules could be utilized to produce an efficient, low voltage OLED.<sup>3</sup> This gained the immediate attention of the display industry. Further attention was gained when Friend and coworkers at Cambridge University demonstrated<sup>4</sup> efficient EL from a spin coated organic polymer. Unlike small molecules, which are vacuum deposited, polymers are

solution processed and may potentially offer an inexpensive route to the manufacture of large area displays. Both these reports led to a period of intense research and development in academia as well as in the display industry. Indeed, due to their potential to usurp market share from more traditional flat panel display technologies such as liquid crystal displays (LCDs), nearly every global electronics firm now has an effort in OLED technology.

## Basic Physics

Organic light emitting devices operate on a principle known as electroluminescence. Electrically injected carriers recombine to generate light. The device physics is best illustrated by examining the simplest type of OLED—one which uses only a single organic layer. The energy level diagram of a typical single layer polymer based light emitting device (PLED) is shown in Fig. 2. The device utilizes ~100 nm of poly *para*-(phenylene vinylene) (PPV) with an ITO anode and calcium cathode. When a forward bias is applied, electrons are injected from the cathode into the lowest unoccupied molecular orbital (LUMO) of the polymer and holes are injected from the anode into the highest occupied molecular orbital (HOMO) of the polymer. Thus, the electrons must overcome the barrier between the Ca Fermi level and the LUMO level of the polymer. Low work function metals such as Mg or Ca are typically used to minimize this barrier and provide for an ohmic contact. Similarly, to ensure ohmic injection of holes from the ITO Fermi level into the HOMO of the polymer, the ITO may be treated in various ways (*e.g.*, exposure to an

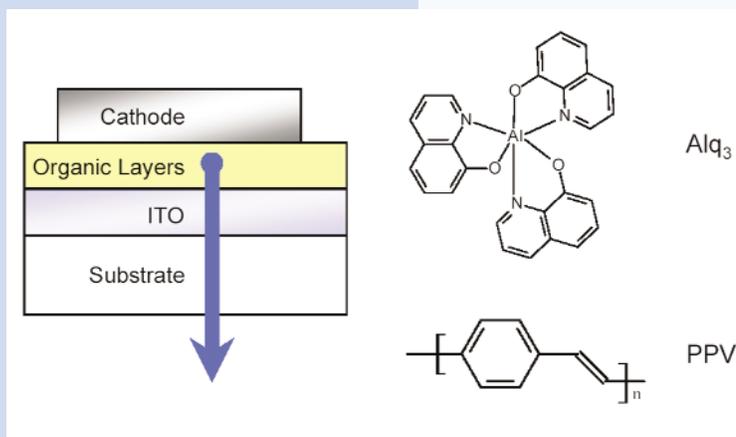


FIG. 1. Cross section schematic of a typical organic light emitting device. Indium tin oxide (ITO) is the anode and a low work function metal is the cathode. Typical organic layer thicknesses are ~100 nm. Shown to the right are a model small molecule: aluminum tris-(8-hydroxyquinoline) (Alq<sub>3</sub>) and a model polymer: poly *para*-(phenylene vinylene) (PPV). Small molecules are typically thermally evaporated and polymers are typically spin cast.

ultraviolet-ozone cleaning) to lower its Fermi level. After carriers are injected, they drift in the presence of the externally applied electric field by hopping from molecule to molecule to the opposite electrode. Due to the intrinsically low mobilities of these materials, the injection and drift of carriers require high electric fields ( $\sim 0.1$  MV/cm). Achieving low voltage operation thus limits the thickness of the organic layers to a few hundred nm. If both charges happen to meet on the same molecule or polymer chain, they may combine to form a molecular excited state known as an exciton. The exciton may then either radiatively recombine to generate a photon or thermally decay. To maximize OLED efficiencies, electrons and holes must be easily injected from the contacts and transported through the organic layers to form excitons. These excitons must then have a very high efficiency of radiative recombination. Thus in addition to choosing optimized contacts for ohmic injection and conductive materials for low voltage transport, materials with high photoluminescence (PL) efficiencies must be chosen to maximize the probability of radiative recombination of generated excitons.

### Progress

While most early small molecule and polymer devices were relatively inefficient and short lived, enormous progress has been made in both the efficiency and lifetime of these devices over the past decade. It was observed that under prolonged operation, black spots would rapidly form over the device active area and drastically reduce device lifetimes.<sup>2</sup> The active materials were found to be sensitive to air and water vapor and degraded rapidly if left unpackaged. Encapsulation of finished devices in an inert gas ambient is a crucial requirement for long lifetimes. Through a combination of materials development and refining of encapsulation techniques, acceptable lifetimes for some commercial display applications are now achievable. However, much work still remains to understand the intrinsic mechanisms of degradation and to increase lifetime for higher brightness applications.

The rapid increase in OLED power efficiencies has been due primarily to three factors: the introduction of new high purity materials with enhanced photoluminescence efficiency and/or charge transport capability, the invention and optimization of new device architectures, and the optimization of carrier injection from contacts.<sup>1,2</sup> Currently, baseline efficiencies required by the display industry (*Editor's note: See Table 1 in previous article on page 22*) are more or less attainable in all three colors in both polymeric and small molecule systems.

For polymer-based OLEDs, the introduction of the polyfluorene family in place of the PPV-type polymers discussed earlier, proved to be a major step forward. Polyfluorenes have excellent film forming properties, are very soluble in organic solvents, and in some cases can have near unity PL efficiency. Recently, these materials have been further optimized and copolymers with hole transporting materials such as the aromatic amines have been synthesized. Green EL in excess of 20 lm/W is readily achievable with these materials.<sup>5</sup>

In addition to polymer materials development, there have been advances in the injection of carriers at contacts. Poor injection from contacts results in inefficient devices due to the higher drive voltage required to attain a given current and the increased likelihood that the electron and hole currents are imbalanced. Such an imbalance reduces efficiency because it implies that one charge carrier is hopping all the way to the opposite electrode without forming a potentially light-emitting exciton. Conducting polymers such as PDOT:PSS (poly(3,4-ethylenedioxythiophene):polystyrene sulfonate) have a Fermi level between that of ITO and the polymer HOMO and thus greatly improve hole injection.<sup>6</sup> Thin PDOT films have been shown to reduce sensitivity to ITO treatment and balance the injection of carriers, resulting in overall improvements in efficiency and yield. At the cathode, reactive metals such as Ca and Mg have been replaced with bilayer cathodes consisting of a thin ( $< 50$  Å) film of either NaF or LiF capped with a film of Al. Explanations for the beneficial effect of these bilayers include Na or Li "doping" of the underlying

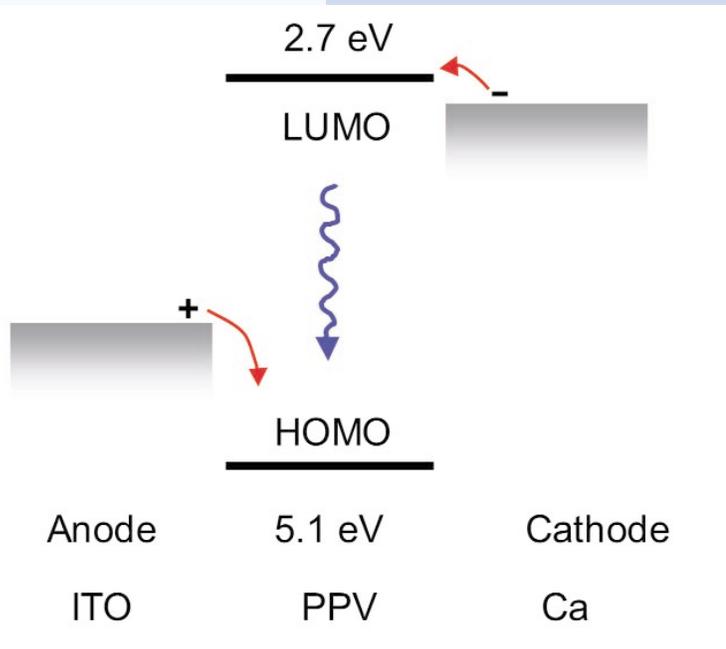


Fig. 2. Schematic energy level diagram of a single layer polymer light emitting device fabricated by spin casting a  $\sim 100$  nm layer of poly para-(phenylene vinylene) (PPV) onto ITO and then thermally evaporating a Ca cathode. Shown are the polymer highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Under forward bias, electrons are injected into the LUMO and holes are injected into the HOMO.

organic layer due to aluminum-induced dissociation of the fluoride and the formation of a dipole layer which favorably adjusts the energy level alignment between the electrode and the organic.<sup>6</sup> The new bilayer cathodes are less prone to delamination and degradation than cathodes made from reactive metals. In addition, these new electrodes lead to improved device reliability and lifetime.

Small-molecule OLEDs have benefited from the same types of contact physics concepts as polymer OLEDs. However, in contrast to polymer OLEDs, where application of multiple solution-processed layers is difficult, small molecule OLEDs can be grown in a variety of different device architectures. Vacuum deposition provides for easy manipulation of layer thickness and placement in a multilayer stack. Depositing materials with different transport characteristics in different layers allows

for another way to improve inefficiencies due to imbalanced injection discussed above. The first efficient small molecule device was based on a single heterostructure: an electron transport layer (ETL) blocked transport of holes and the hole transport layer (HTL) blocked transport of electrons. Therefore excitons are forced to form at the interface between the two layers without “leakage” of holes or electrons to their opposite electrodes. A way to further improve upon this bilayer structure is to dope small quantities of very high PL efficiency materials in the transport layers near the HTL/ETL interface.<sup>2</sup> As illustrated by the energy level schematic of an optimized small molecule OLED in Fig. 3,<sup>7</sup> small quantities of a guest molecule are doped into the ETL (CBP) near the interface with the HTL. After either direct trapping of carriers or nonradiative transfer of excitons from the transport layers, these guest molecules very efficiently radiatively recombine and may more than double the OLED device efficiency. More importantly, vacuum deposition allows for the separate optimization of different functions such as transport and

emission. This has placed the focus on developing low molecular weight materials independently for transport and luminescence and allows for borrowing of concepts from inorganic LEDs such as energy level engineering. In inorganic semiconductor LEDs and lasers, materials with larger bandgaps are used to transport carriers to materials with smaller bandgaps, where confinement and luminescence occurs. So in addition to using a bilayer device as discussed above, separate electron and hole blocking layers are inserted on either side of the recombination zone to further confine carriers and excitons. This concept is illustrated using the energy level diagram shown in Fig. 3. The deep HOMO of the small molecule hole blocking layer, bathocuproine (BCP) not only confines holes but also confines excitons to a thin region near the interface of the HTL and ETL.<sup>7</sup> Blocking layers such as this are especially necessary when the exciton diffusion lengths are large, in order to prevent quenching at electrodes.

### Phosphorescence

Even though highly fluorescent dyes increase EL efficiencies for small-molecule OLEDs, they only harness a fraction of all electrically generated excitons. Two types of excitons are formed when electrically injected carriers recombine: singlet excitons with total spin  $S = 0$  and triplet excitons with total spin  $S = 1$ . Since the ground state of organic molecules has  $S = 0$ , and the relaxation of a molecule through the radiative recombination of an exciton must conserve spin, fluorescent emission from singlet excitons is the only allowed process that generates photons. Hence, for typical fluorescent-based OLEDs, all triplet excitons are wasted. For small-molecule devices, it is believed that only 25% of the emissive singlet excitons are formed during electrical excitation.

However, some materials do exhibit light emission from triplet excitons. In these materials, the singlet and triplet states are mixed and hence the excited triplet states share some singlet character and radiative decay to the ground state is allowed. This process is known as phosphorescence. Adding a heavy metal atom such as iridium to an organic molecule increases the spin-orbit coupling that mixes singlet and triplet excited states allowing for efficient radiative decay of triplet excitons.

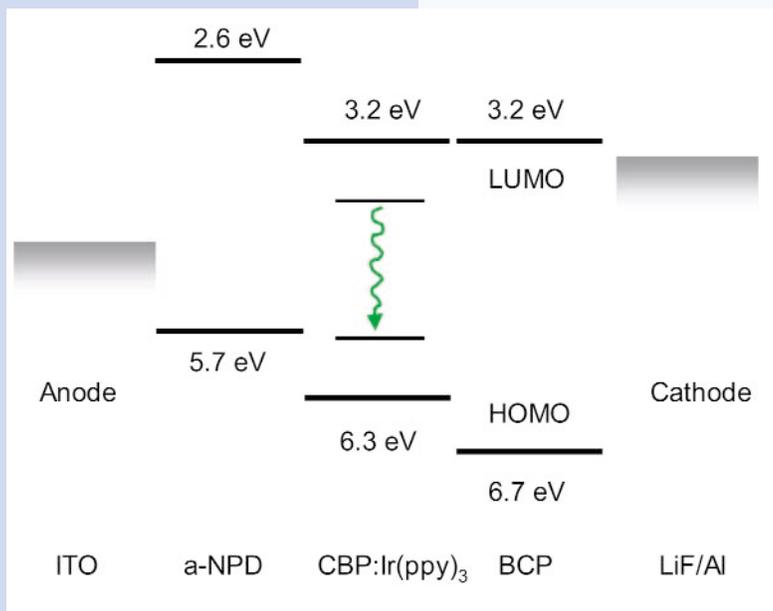


Fig. 3. Schematic energy level diagram of an optimized small molecule OLED employing the phosphorescent complex: fac tris(2-phenylpyridine) iridium [Ir(ppy)<sub>3</sub>] doped into a 4,4'-N,N'-dicarbazole-biphenyl (CBP) host. The hole transport layer is a thin film of 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino] biphenyl ( $\alpha$ -NPD). A molecule with a large HOMO-LUMO spacing is used here as both a carrier and exciton blocking layer: 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine, or BCP). A bilayer cathode consisting of a thin ( $< 10 \text{ \AA}$ ) layer of LiF, followed by a thicker layer of Al, is used to efficiently inject electrons. The emission between the two dashed lines within the CBP energy level gap schematically depicts radiative recombination of both singlet and triplet excitons on the Ir(ppy)<sub>3</sub> molecule.

The energy level schematic of an OLED employing an iridium-based phosphorescent small molecule is shown in Fig. 3. Here, two ETL layers are used—one (CBP) hosts the phosphorescent iridium complex and one (BCP) acts solely as a hole (and exciton) blocking layer. Upon injection, holes are transported in the HTL and recombine with the electrons that have been injected into the hole blocking layer and have drifted to the CBP ETL. Both singlet and triplet excitons are formed in the CBP host and then both types of excitons are transferred nonradiatively to the emissive state of the iridium complex. This state then emits light through phosphorescence. The net effect is that both the singlet and triplet excitons created in CBP are utilized for light emission. While purely singlet exciton emission would imply an upper limit on the internal quantum efficiency of ~25 %, nearly 100% internal efficiency OLEDs have recently been demonstrated employing this iridium complex.<sup>8</sup> This clearly demonstrates the potential of high efficiency OLEDs based on phosphorescence.

Although there is some controversy regarding the fraction of emissive singlet excitons formed in polymeric systems,<sup>9</sup> efforts have nevertheless been made to blend efficient phosphorescent small molecules into polymers to try to make use of the triplet excitons.<sup>10,11</sup> To date, the observed efficiencies in these hybrid systems remain below those described above, presumably due to incomplete energy transfer and lack of exciton confinement. However, with further materials development, the efficient harnessing of triplet excitons with PLEDs should be possible thereby potentially enabling solution processible devices with 100% internal efficiency.

A problem common to all OLEDs, particularly phosphorescent OLEDs is the rapid drop in power efficiency with increasing brightness due to either second-order excitonic processes or ohmic losses in the transport layers or at the contacts. These ohmic losses have typically limited small molecule OLED drive voltages to higher than 5 V. Recently however, doping transport layers with either donor or acceptor type materials has led to significant increases in film conductivities and hence concomitant decreases in drive voltage: display brightnesses are now achievable at 2.6 V in the green. Starting with the OLED shown in Fig. 3, doping the electron transport layer with alkali metals such as Li and doping the hole transport layer with a strong organic acceptor such as F<sub>4</sub>-TCNQ (tetrafluorotetracyanoquinodimethane) was used recently to demonstrate<sup>12</sup> OLEDs operating with efficiencies in excess of 25 lm/W at brightnesses required for lighting applications—10X that required for display applications. Over the next few years, it is likely that higher efficiencies at high brightness will be demonstrated as more research groups begin to develop and optimize new device architectures that exploit this doping concept.

### Emerging Applications: OLED Displays

Current estimates place the value of the rapidly growing display market at ~\$100 Billion by 2005. The development of organic light emitting devices as a potential replacement for liquid crystal displays (LCDs) has been the principal focus of much of the research in this field over the past decade. As active emitters, OLEDs do not require the heavy, environmentally unfriendly mercury containing backlights found in LCDs. Further, higher contrast, faster response OLED based displays can offer viewing angles of up to 160°, far greater than LCDs. Pioneer introduced the first commercially available OLED based display in 1997. It was a passive matrix display used for car radio faceplates. These small molecule based displays were also found in Motorola cellular phones by 2000. More recently, the first commercially available polymer LEDs have been sold in a simple passive matrix scheme as displays in MP3 players made by Delta Optoelectronics and in a well publicized Phillips electric razor displayed prominently as James Bond's newest gadget in the movie "Die Another Day." The advantages of OLED based displays are more apparent in larger sizes—particularly in full-color high-resolution active-matrix (AM) displays—where the OLED saturated emission results in more vibrant images than possible with LCDs. While prototype AM displays based on polymers and small molecules have been available for several years, the first commercially available AM OLED display was just recently announced by Kodak for use as a display in digital cameras and is shown in Fig. 4. The approximately 1/4 VGA, 2.2 inch diagonal full color display promises to be the first in a number of thin, ultra-lightweight, bright OLED based displays. While small



FIG. 4. A digital camera incorporating the first commercially available active matrix OLED display. Picture courtesy of Eastman Kodak Company.

molecule AM displays are patterned using shadow masks, full color AM polymer displays are generally patterned using inkjet printing to locally deposit films of the different emissive materials. Since they are solution processed, it is challenging to pattern polymers using other techniques. However, it was recently demonstrated<sup>13</sup> that a new class of photochemically cured polyfluorenes can be crosslinked and made insoluble. After crosslinking, the unwanted polymer is rinsed away to form high resolution pixels. These new crosslinked polyfluorenes are patterned using standard semiconductor processing techniques and may prove to be very useful for high resolution solution processible AM displays.

### Future Applications: Lighting

The rapid progress in efficiency and performance demonstrated by OLED technology over the last decade has caused many companies to consider OLEDs as a potential solid-state light source for lighting applications. In terms of application potential, OLEDs nicely complement inorganic LEDs—a technology more often associated with solid-state lighting. In particular, since inorganic LEDs are bright point sources of light, they are naturally suited for applications such as spot or task lighting that require spatial control over the illuminating beam. In contrast, OLEDs represent a diffuse source of light and so are naturally suited to large area general-lighting and signage applications where, for instance, fluorescent lighting is used today. Another attractive feature of OLED technology for the lighting industry is the potential for extremely low cost “newspaper-like” processing due to the fact that the active organic layers are amorphous and hence do not require the precise epitaxial growth needed to fabricate inorganic LEDs. Efforts are already underway to build OLEDs on mechanically flexible substrates using roll-to-roll processing. If such low-cost methods prove practical, completely new types of flexible “wrap-around” lighting designs and products will be enabled.

The performance of OLEDs is already adequate for many specialty lighting applications. It is expected that such products will be produced once the OLED manufacturing infrastructure, which is just beginning to be developed for displays, becomes more mature. Nevertheless, in the research world, effort is now concentrating on the big prize—general illumination. Here the goal is to displace fluorescent bulbs as the premier diffuse lighting technology. Most effort to date has concentrated on showing that OLEDs can be designed to generate white light with illumination-quality equal to, or better than, what is commercially available today with fluorescent technology. There are many degrees of freedom in designing an OLED and so numerous approaches to generating white light have been demonstrated over the years. Three promising schemes that have specifically addressed the issue of illumination-quality

are: designing a single emissive dopant that emits the correct spectrum,<sup>14</sup> utilizing multiple emissive dopants in multiple layers of a device,<sup>15</sup> and applying phosphor down-conversion materials to a blue-emissive OLED.<sup>16</sup> Figure 5 depicts an illumination-quality device made at GE Global Research using the down-conversion approach. The device provides approximately 70 lumens of white light at 4000 K with better color rendition than fluorescent lighting. Note that all of the light in this scene is provided by the OLED.

Formidable technical challenges need to be overcome before OLED technology can overtake fluorescent technology for general illumination. For instance, white light device efficiency needs to be increased by more than a factor of 10 over what has been achieved today and lifetimes on the order of 20,000 hours are needed at brightness levels that are a factor of 10 higher than what is required for typical display applications. In addition, general lighting cannot be expensive and so the promise of low-cost roll-to-roll manufacturing must be realized. Achieving these goals will require the research community to continue the rapid rate of technology progress through the development of new strategies in OLED materials, device structures, and large area designs. If successful, “lighting wallpaper” may become a reality or, perhaps more intriguing, the distinction between an information display and a light source may disappear. ■



*FIG. 5. Past and future lighting technologies. A white light OLED research device made at GE Global Research, which provides 70 lumens of illumination with a color temperature of 4000 K, a color rendition index of 90, and an efficiency of 7 lumens per watt.*

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