DISPLAYS BASED ON ORGANIC THIN FILMS

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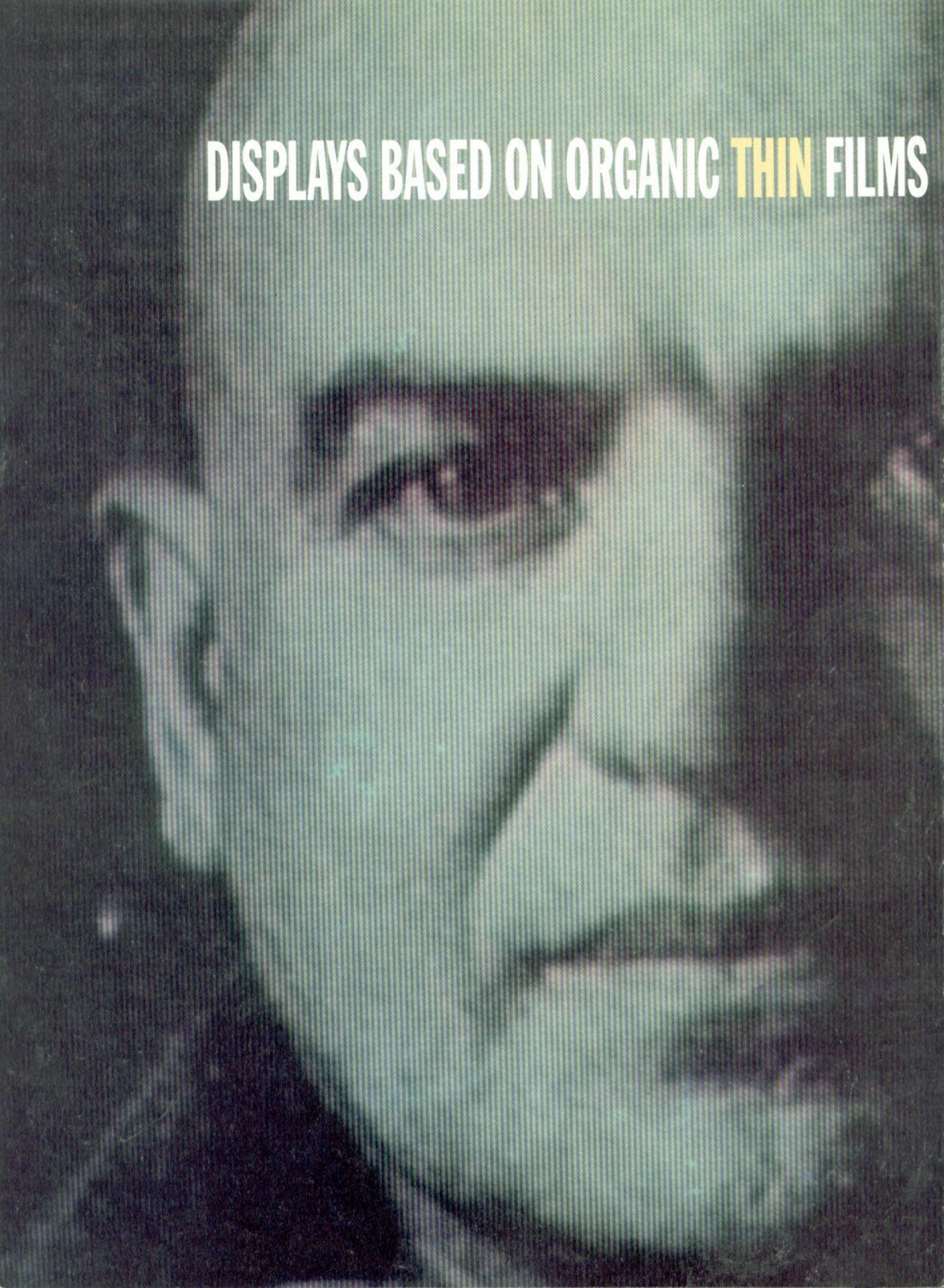
Snapshot: The authors describe the basics of organic thin film

and how they can be transformed into commercial displays.

Note: This article will be featured at the OSA Annual Meeting in a symposium sponsored jointly with the Organic Thin Films Topical Meeting (Tuesday, September 12) in Portland, Oregon.

Organic thin films have become increasingly important in recent years for both fundamental scientific reasons and because of their technological potential. Some of the most important applications of organic thin films are in information display systems. The increasing importance of video and graphic displays in communication and information processing make display technology a key element. The current market is very large and is growing rapidly as video displays migrate from television to computers to telecommunication.

Because of these markets, high information content flat panel displays are in great demand. These fall into two categories: emissive, such as plasma and electroluminescent displays, and non-emissive, such as liquid crystal displays. The most promising emissive technology today is electroluminescent polymers. The most rapidly growing[1] non-emissive technology uses liquid crystals.

Liquid crystals are anisotropic fluids, whose optical properties and ready response to external fields make them ideally suited for display applications. They exhibit many different phases. In the simplest phase—nematic—rod- (or disk-)

like molecules tend to align in the same direction, along the so-called nematic director. Liquid crystal displays make use of three properties of nematics:
- birefringence,
- elastic response to orientational deformations, and
- tendency to align parallel to an applied field.

To make a switchable device, the orientation of the molecules—that is, of the nematic director—is determined at the boundary surfaces by a surface alignment layer. When a field is applied, the liquid crystal aligns with the field as much as the alignment layer and elastic effects allow. When the field is turned off, the elastic and surface torques restore the original configuration. The alignment layer is usually a thin organic film, which plays an essential role in the operation of the display.

Typical display cells consist of a liquid crystal slab sandwiched between parallel glass plates. To apply voltage to switch a pixel, the plates are coated with a transparent conducting film, usually indium tin oxide (ITO). In twisted (TN) and supertwisted (STN) nematic displays, the ITO layer is covered by an alignment layer, which ensures that the director aligns along a chosen direction on the surface. The direction of orientation on the two plates is different, the director twists through an angle of 90° in the case of TN and 180-240° in the case of STN cells. In active matrix (AMLCD) displays, a thin film transistor or some other active device is situat-
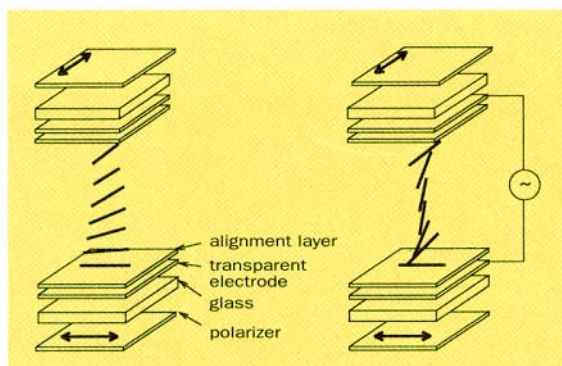

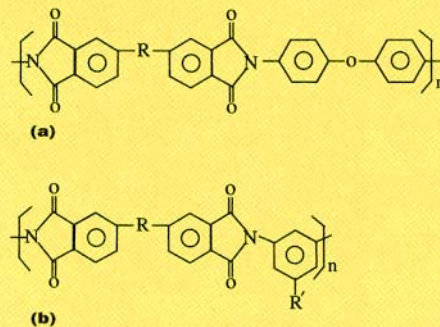**Figure 1.** Schematic of TN cell showing the effects of an applied voltage.

Figure 2. Chemical structure of (a) main-chain and (b) side-chain polyimide.

Alignment layers are typically ~600Å thick in nematic displays. A frequently used material is polyimide (such as Dupont 2555), but other organic materials such as PMMA poly(methyl methacrylate), PVF, poly(vinyl formal), and nylon can be used. The chemical structure of polyimide is shown in Figure 2. The alignment layers are formed by spin coating ITO-coated glass substrates with polyimide dissolved in an organic solvent such as NMP (n-methyl-2-pyrrolidone). The spin-coated layer is dried and baked, then it is mechanically buffed by a rotating drum carrying velvet cloth. The fibers of the cloth create grooves in the polyimide layer and align the polymer chains. Although it was originally suggested that the grooves are responsible for aligning the liquid crystal, it now appears[5] that dispersion forces between the liquid crystal molecules and the aligned polyimide are primarily responsible for the creation of an easy axis for the director alignment. The direction of the director on these buffed surfaces is slightly out-of-plane; these few degrees of tilt[6] break inversion symmetry and hence play a key role in switching.

ed at each pixel to give better control of the applied field. The cell is placed between crossed polarizers, as shown in Figure 1. Without an applied voltage, the polarization of light follows the nematic director as light traverses the cell, and the pixel is transparent. If a sufficiently large voltage is applied, the director is normal to the plates, the polarization of light is no longer rotated, light is absorbed by the second polarizer, and the pixel is dark. A description of liquid crystal displays appeared recently in *Optics & Photonics News.*[2]

Although both the liquid crystal and the polarizers are organic materials, we focus here on the role of the thin organic alignment layer. In contrast to conventional materials, nematic liquid crystals exhibit different effects depending on sample thickness.[3] In thick samples surface effects dominate, while in thin samples, bulk effects dominate. The thickness of typical display cells is ≈5 μm, and on these length scales, in the absence of external fields, surface interactions govern the configuration of the bulk. The alignment layers, whose job it is to ensure director alignment at the surface, thus play a crucial role in determining the optical response of display cells.

The first thorough review of alignment techniques is by Cognard.[4]

Figure 4. Surface stabilized cholesteric display[20] produced at the Liquid Crystal Institute. Electronic tablets such as this may become the newspaper of the future.

Although used in the manufacture of all conventional LCDs, mechanical buffing has its drawbacks. Properties of the fabric change with time due to fiber wear and loss in the buffing process. Dust particles are generated, and electrostatic charge build-up can damage the thin film transistors in active matrix devices. The buffed surfaces show, on occasion, unacceptable irregularities in director alignment. Due to the high cost and long throughput times (typically several weeks) of AMLCDs, the resulting decrease in yield becomes a problem.

A number of alternatives to mechanical buffing have emerged recently. First, displays have been developed that do not require alignment of the director in the plane of the substrate. Amorphous[7] TNLCDs do not require uniform director alignment at the surface; so although a polyimide alignment layer is used, buffing, is not necessary. Second, polarized light has been used in a variety of ways to alter the structure of the alignment layer. One method involves the photopolymerization of the alignment layer by linearly polarized UV light. In materials, such as polyvinyl cinnamate,[8] irradiation by polarized light results in a preferred direction of bond formation, the creation of a unique direction in the polymer film and hence the establishment of an easy axis for the alignment.[9] Conversely, irradiating a fully polymerized polyimide alignment layer with polarized UV again results in the creation of an easy axis, presumably due to opening of bonds with a given orientation.[10]

Perhaps the most interesting effect of optical fields on the alignment layer involves photoinduced conformational changes. Photoinduced optical anisotropy—the Weigert effect[11]—has been known for some time. In bulk nematics, light induced conformational changes of azo-compounds can dramatically change the liquid crystalline behavior.[12] Recently, Gibbons and co-workers found[13] that if an azo-dye is dissolved in the polymer forming the alignment layer, irradiation of the alignment layer with polarized light aligns the liquid crystal in contact with it. This mechanism consists of two steps: orientation of the dye in the polymer by polarized light, and the subsequent alignment of the liquid crystal by the oriented dye. In the alignment layer, dye molecules in the *trans* state—those with a transition dipole moment along the polarization direction—are preferentially excited into the *cis* state. These *cis*-isomers undergo orientational diffusion, and eventually relax back to the less diffusive *trans* state. This "orientational hole burning," the de-population of the state where the transition moment is along the polarization direction, gives rise to a net orientation of dye molecules. The interaction of the dye and liquid crystal, presumably via dispersion forces, gives rise to the director orientation. The alignment is stable, and can be rewritten indefinitely by subsequent irradiation.

This process enables "optical buffing" of the alignment layer, and, since the easy direction can be changed

locally[14-15] it allows individual pixels to be re-written. This is important not only for correcting misalignment, but also for the production of multi-domain displays,[16] where the director in adjacent pixels has a different orientation. Since director orientation can be controlled separately for each pixel, high resolution continuous gray scale images can be written into TN cells. Figure 3 shows a picture generated using this method. The alignment layer was written with a cw argon laser at 514 nm; the 50 μm thick cell was filled with a nematic liquid crystal mixture.

Liquid crystals in a variety of phases other than nematic are being developed and used for displays. Ferro-[17], antiferro-[18] and ferri-[19] electric liquid crystals are of particular interest; alignment layers here also play an important role.

Cholesteric liquid crystals are nematics whose molecules are chiral; that is, they have a left- or right-handed twist. Due to this chirality, the director rotates in space as a function of position, in a direction perpendicular to the director, tracing out a helix. Bragg reflection from this periodic structure can cause a uniform cholesteric to appear brightly colored. If the cholesteric is not uniform, but consists of random domains, the material will scatter light. Surface alignment layers can make both the reflective uniform state and the scattering focal conic state stable. Such surface stabilized cholesteric displays, using polyimide or PMMA alignment layers, have been recently developed.[20] Here the preferred director alignment is perpendicular to the normal surface. These devices show particular promise, since they do not require polarizers or backlights, and, since they are bistable, they do not need to be refreshed. They may also be made on a polymer substrate, allowing mechanical flexibility. Figure 4 shows a surface stabilized cholesteric display. Cholesterics may also be stabilized by a polymer network in the bulk. In addition to stabilizing the structure, such a network can improve the optical properties and the drive voltage requirements. These materials are also candidates for high-density information storage; Figure 5 shows a laser-written image in a polymer stabilized cholesteric, doped with an anthroquinone dye.

Thin organic films as alignment layers are integral components of liquid crystal displays. A wide variety of materials, whose liquid crystal aligning properties can be controlled, are being developed for this purpose. Such films are expected to make possible new types of liquid crystal displays, as well as other surface-controlled optical structures.

Organic light emitting diodes

While liquid crystal displays have found widespread application where reflected or transmitted light is avail-

Figure 5. Laser-written image (2cm × 2cm) of Telly Savalas written in a polymer stabilized cholesteric cell.

able, self-luminous displays are necessary or preferable in many situations. To this end, organic light emitting diodes (OLEDs) are being vigorously investigated. For example, high performance, low cost, flat panel emissive color displays would quickly displace cathode-ray tube television and computer monitors. In LEDs, electrical stimulation of the LED structure leads to a colorful emission of light. By combining appropriate red, green, and blue emitting LEDs, one can produce full color displays. A major challenge in the development of LED displays using any semiconductor material (including organics) is producing LEDs with the proper spectral content to generate pleasing and realistic colors. A key advantage to organic materials is the ability to chemically tailor them through a wide range of structures and emission spectra. Another advantage of organic and polymeric LEDs over other material approaches such as III-V and II-VI semiconductors is their potential for low-cost processing, fabrication of large area displays, and mechanical flexibility. There are currently two main approaches to the processing of organic LEDs: vacuum thin-film deposition of organic molecules and spin-coating of organic polymers. Vacuum thin film deposition is more controllable than spin-coating, but also more expensive. The optimization of each approach relative to controllability, cost, and performance will determine which is more commercially viable; it is still too early to tell.

Organic LEDs are multilayer structures, as shown in Figure 6, composed of two electrodes with one or more organic layers between them. The negative electrode injects electrons into the sample and the positive electrode draws electrons out, although it is customary to say that the positive electrode injects holes into the sample. The electrons and holes must then be transported to an emissive layer where they can form a localized bound state with each other known as an exciton. Exciton formation is aided by the presence of traps that help bind the excitons. The exciton then decays, and in doing so, emits light. The functions required, then, are injection, transport, exciton formation, and exciton decay. The structure must be tailored to promote all of these functions. Injection is generally controlled by the relative electron affinity between the electrodes and the device. Many metals will easily inject holes into organics since they have a higher electron affinity. The transparent conductor ITO, is commonly used to inject holes and to transmit the emitted light. Recently, enhanced performance was observed using a polymeric electrode based on polyaniline (PANI).[21] The negative electrode must have a lower electron affinity than the polymer, a condition more difficult to achieve. Calcium is often used, but it is quite reactive and limits the reliability of the device. High electron affinity polymers have been made more recently which allow the use of less reactive metals such as aluminum as electrodes.[22]

Once the electrons and holes are injected into the device, the organic materials provide for transport, as well as exciton formation and decay. Molecular materials, first studied at Eastman Kodak,[23] are generally based on aluminum *tris*-8-hydroxyquinline (Alq$_3$). In
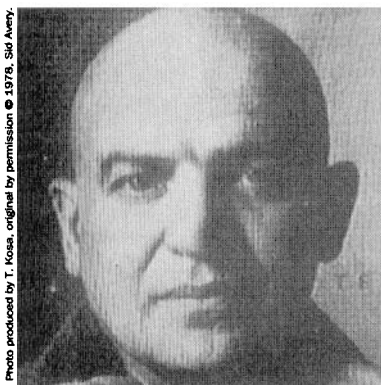
these devices, a hole transport material such as diamine is vacuum deposited as a layer tens of nanometers thick on top of the ITO electrode. The emitting layer, such as Alq_3, is vacuum deposited on top of that, and the structure is then covered by the negative electrode material. The molecular structure of Alq_3 is shown in Figure 7(a). A hole transport layer is necessary because Alq_3 is not an efficient hole transporter. Since the first reports, chemical modifications have been made to improve efficiency by lowering operating voltages, and to produce the requisite colors.[24] Though emission is often too broadband for proper color saturation, recent work has shown that multi-layer Fabry-Perot structures can be fabricated that allow tuning of the color output by varying the thickness of the device.[25] Molecular OLEDs producing several lumens/watt (similar to a light bulb) have been produced with lifetimes in thousands of hours.
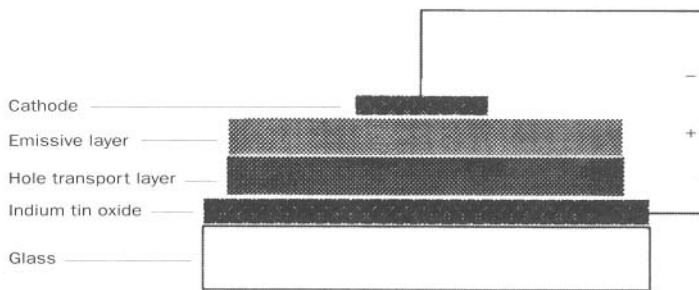
Figure 6. Structure of organic light emitting diode. For PPV polymer devices, the hole transport layer is absent.

Polymer materials, mostly based on poly-p-phenylenevinylene (PPV), were first studied at Cambridge.[26] The structure of PPV is also shown in Figure 7(b). These polymers can be spun or otherwise cast onto a substrate. In this case, the PPV acts as a hole transport agent as well as the emissive layer, thus eliminating the need for an additional layer. The polymer approach appears to be lower cost than vacuum deposition; however, the performance of polymer LEDs lags behind that of molecular films. As in the case of vacuum-deposited molecular materials, chemical modification of the polymer has produced variations in color. Alternating blocks of polymer fragments or oligomers have been used to do this.[27] The addition of electron acceptors shifts the normally green emission toward the blue, while electron donors shift it toward the red. Colors from blue to orange have been produced. Though efficiencies of a

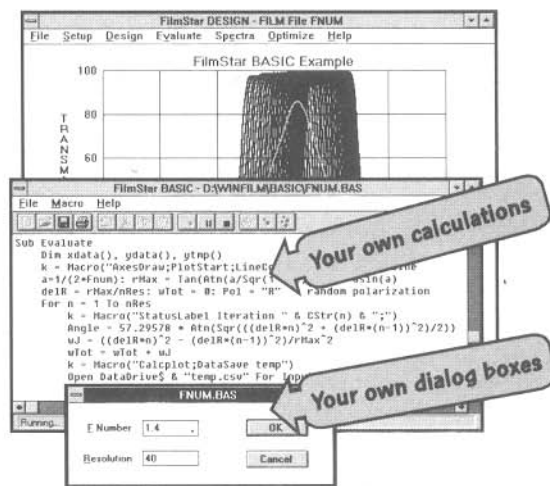few percent or a few lumens per watt have been achieved in polymers, their reliability is considerably poorer than that of molecular materials. Increasing the efficiency reduces the heat generated, thus improving reliability as well as performance.
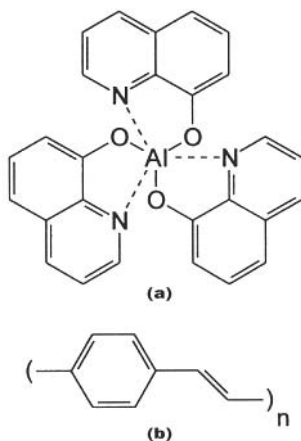
OLED challenges

While the potential market for low-cost, large area luminous displays is vast, a number of problems with OLEDs must be overcome before their performance is appropriate. These problems include issues of reliability, efficiency, and color. The electrochemistry involved in the degradation of devices is poorly understood, and in PPV, lifetimes are limited to hundreds of hours. In addition, PPV has a rather short shelf-life which proper encapsulation may improve. The chemical modifications used to tune the color of emission also affect efficiency and operating characteristics, such as the driving voltage. Since efficiency is related to reliability, the outstanding issues are interrelated and will require certain trade-offs. However, the multitude of possible organic structures provides rich possibilities for further improvements.

Figure 7. Molecular structure of (a) aluminum *tris*-8-hydroxyquinline (Alq₃) (b) poly-p-phenylenevinylene (PPV).

The current properties of organic LEDs fall short of requirements for color video display applications in the near term. However, less demanding applications such as appliance displays may be much closer to realization. It is possible that products from both polymer and molecule OLEDs will appear within a year.[28] It should be noted that in these lower-end applications, polymers will be competing with existing technology such as semiconductor LEDs and liquid crystal displays. One property which makes OLEDs suitable for these types of applications is the mechanical flexibility of polymeric LEDs. This allows the possibility of curved or even folding displays. Another application, which dovetails with the first part of this article, is the use of large area OLEDs as backlights for liquid crystal displays. The broadband emission of OLEDs may be well suited for this application.

A great deal needs to be done to fully develop organic LEDs. The field has been expanding rapidly with laboratories around the world entering. This bodes well for further progress in this emerging technology as new chemists, physicists, device scientists, and engineers turn their attention to this approach to display technology. The vastness of this potential market will mean that no stone (or film) will go unturned in the search for high-performace, low-cost emissive display technology.

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