Incorporation of Photoluminescent Polarizers into Liquid Crystal Displays

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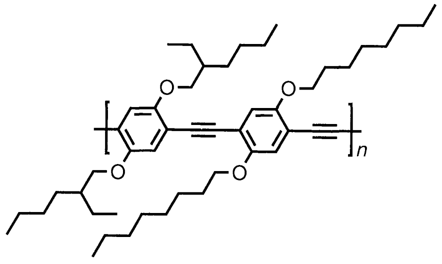
Liquid crystal displays, the dominant flat panel display technology, are limited in brightness and energy efficiency because of the use of absorbing polarizers and color filters. Liquid crystal–based photoluminescent display devices have been fabricated that use thin, polarized photoluminescent layers that have highly anisotropic absorption or emission. These layers both polarize light and generate bright color. This approach can simplify device design and substantially increase device brightness, contrast, efficiency, and (in specific configurations) viewing angle.

Research in the field of flat panel displays now encompasses inorganic (*1*) and organic (*2*) electroluminescent (EL) light-emitting devices, plasma display panels, and vacuum fluorescent displays. Nonetheless, liquid crystal displays (LCDs) have maintained their dominant position in this field. The main advantages of LCDs are their low power consumption, low-voltage operation, and semiconductor compatibility. However, their limited brightness and energy efficiency, as well as their often unsatisfying viewing angle, leave ample room for further improvement (*3*). The severe brightness and efficiency limitations of LCDs arise chiefly from the use of dichroic sheet polarizers and absorbing color filters, because these elements convert into thermal energy, and thus lose a large fraction (>80%) of the incident light (*3*).

The use of photoluminescent (PL) materials, which act as "active" color filters, could enhance the visual performance of LCDs (*4–6*). Several ways exist to incorporate luminescent materials into LCDs, including the use of fluorescent LCs or the dissolution or dispersion of luminescent molecules in a conventional LC layer (*4*), or the application of PL plates (*5*) or front-face screens (*6*). However, the proposed devices suffer from a number of drawbacks related to the limited stability of the fluorescent dyes or LCs, the difficulty of producing pixilated devices, depolarization effects, or the required thickness (>1 mm) and (large) area of the luminescent layer (*5*). Here, we introduce a design for LC-based PL display devices that comprise one or more thin, highly linearly polarized PL layers. These polarized PL layers are characterized by either anisotropic absorption or anisotropic emission or both, and are efficient in linearly polarizing light and generating bright colors.

Uniaxially oriented PL materials usually exhibit anisotropic, or linearly polarized, absorption and emission. This phenomenon, known to occur in inorganic crystals for more than a century (*7*), has been reported for uniaxially oriented films of conjugated luminescent polymers (*8*). However, the use of such (polymeric) polarized luminescent layers has been predominantly limited to EL light-emitting devices (*9*), and the PL properties of oriented, conjugated polymers have been little exploited in devices.

We used polarized PL layers based on highly uniaxially oriented blends of EHO-OPPE, a poly(2,5-dialkoxy-*p*-phenylene-ethynylene) (PPE) derivative substituted with linear and sterically hindered alkyloxy groups in an alternating pattern (Scheme 1), and ultrahigh molecular weight polyethylene (UHMW-PE). This PPE derivative (number-average molecular weight, 84,000 g mol^{-1}) (*10*) offers an ideal matrix of properties with respect to the preparation of polarized PL layers (*10–12*). Oriented blends containing 2% (w/w) EHO-OPPE and the matrix polymer UHMW-PE were prepared by solution casting and subsequent tensile drawing in the solid state (*13*). This process not only leads to highly oriented, strongly luminescent, and extraordinarily stable PL layers, but also produces mechanically coherent, polarized PL layers of minute thickness (<5 μm). The yellow-green light–emitting PPE-based polarized PL layers we used were about 2 μm thick [the typical thickness of the LC layer in standard devices is around 10 μm (*3*)] and were characterized by a high degree of polarization in both absorption and emission, as shown by the dichroic ratios (defined as the ratios of the integrals of the respective transitions) of 15 in absorption and 22 in emission (Fig. 1). In addition, we used orange-red light–emitting polarized PL layers based on blends of 1 % (w/w) poly(2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylene-vinylene) (MEH-PPV) (*14*) and UHMW-PE that were prepared in analogy to the PPE-based polarized PL layers.



Scheme 1.

In our backlit display devices, the light used to photoexcite the PL layer [a 4-W ultraviolet (UV) lamp emitting at 365 nm], or light emitted from the PL layer, can be switched by a twisted nematic (TN) electro-optical (EO) light valve (Fig. 2). These are commercial devices and are not optimized to the absorption and emission characteristics of the PL layer. Depending on the selected

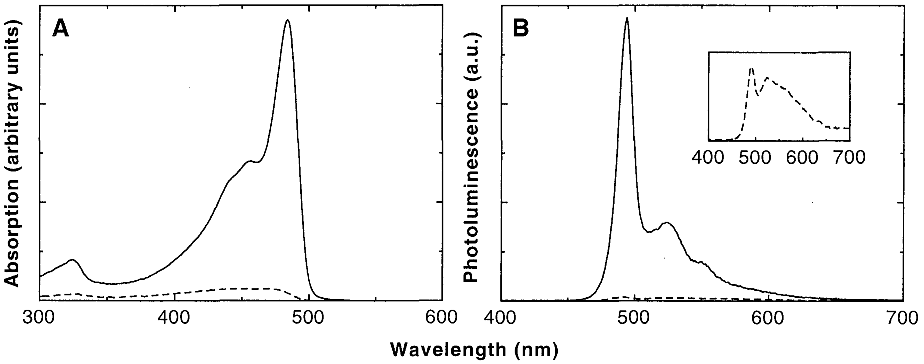


Fig. 1. Polarized absorption (**A**) and photoluminescence (**B**) of an oriented film (draw ratio, λ = 80) of a 2 weight % EHO-OPPE–UHMW-PE blend. The spectra were recorded with polarizers oriented parallel (solid line) and perpendicular (dashed line) to the orientation direction of the polymer blend films. The inset in (B) shows at a magnification of 70 the spectrum recorded perpendicular to the orientation direction.

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configuration, the predominantly relevant polarization characteristic of the polarized PL layer is a high degree of anisotropy in either absorption or PL emission. A monochromatic device structure (device A, Fig. 2A), in which light emitted from the polarized PL layer is switched, consists of a linear polarizer (here used as an analyzer), an EO light valve, the polarized PL layer, and a light source. The light radiated by the light source is at least partially absorbed in the polarized PL layer, so that polarized light is emitted. This emitted light either passes the combination of EO light valve and polarizer (switching state "bright") or is blocked (switching state "dark"). Maximum contrast is obtained when (i) the polarized PL layer is characterized by a high dichroic ratio for PL emission, and (ii) the portion of visible light that is emitted by the light source but is not absorbed by the polarized PL layer—and thus exits the device in the direction of the viewer—is minimal. This can be achieved by different means, for example, by using an additional cutoff filter or a UV light source. In the latter case, the portion of UV light that is not absorbed by the polarized PL layer may be absorbed by the EO light valve and the polarizer, because both these elements are usually absorbing in the UV regime.

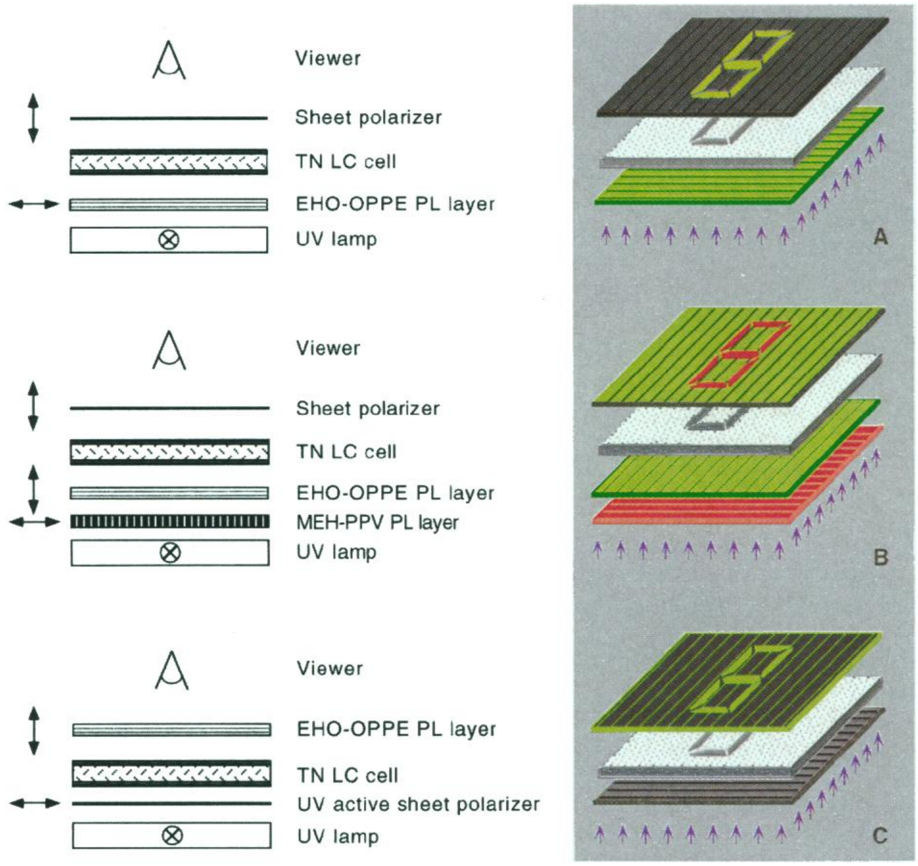

Fig. 2. Schematic structures of PL display devices. (**A**) Device in which the light emitted by the polarized PL layer is switched. (**B**) Bicolor device in which the light emitted by the polarized PL layer is switched. (**C**) Device where the UV excitation light is switched. Arrows at the left indicate the polarization directions of the respective elements. Devices A and B constituted a commercially available, standard TN cell fitted with a linear sheet polarizer. Device C was based on a laboratory UV-active TN cell and a UV-active sheet polarizer (Polaroid HNP-B) producing linearly polarized light. All devices used a Bioblock UV lamp (VL-4LC). Absolute brightness was measured with a Minolta LS 100 luminance meter fitted with 110 and 122 close-up lenses.

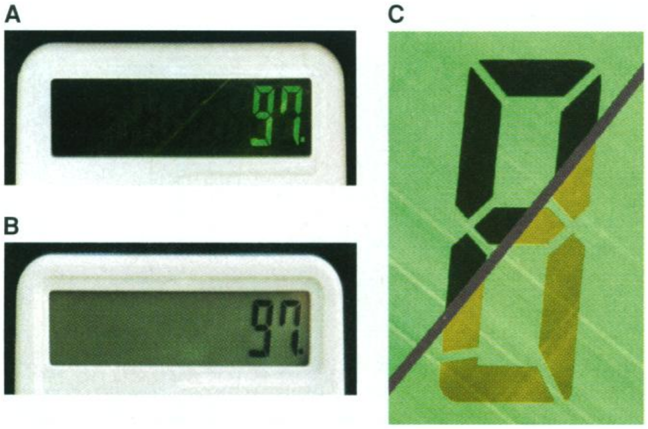

Fig. 3. Photographs of (**A**) a PL display device like that shown in Fig. 2A and (**B**) a similar commercial, direct-view LCD under identical ambient conditions. (**C**) Photograph of a bicolor PL display device like that shown in Fig. 2B. For ease of comparison, the MEH-PPV–based polarized PL layer was omitted in the upper left part of the display where the device consequently operates similarly to the one shown in (A), but, because of the different orientation of the EHO-OPPE–based PL layer, reveals inverted switching states.

Switching of device A was perceived by eye as a change from a very bright yellow-green to almost completely dark (Fig. 3A) and was measured to be 30 and 4 cd m^{-2}, respectively, for the bright and dark states. A similar commercial direct-view LCD operating in reflective mode (Fig. 3B) had values of 17 and 7 cd m^{-2}, respectively, under identical ambient conditions. The apparent limitations of device A are clearly related to the low optical density of the PL polarizers (isotropic absorption of the PL polarizer used = 0.04) at the excitation wavelength and also to the experimental conditions, in particular the reflection of ambient light in the dark state. Thus, brighter devices can be obtained by increasing the optical density of the PL polarizer. This was also demonstrated by using an EHO-OPPE–based PL polarizer of increased (but still far from optimized) optical density (isotropic absorption = 0.18 at 365 nm), which yielded a device like that shown in Fig. 2A but exhibiting a bright state of 65 cd m^{-2}.

In a bicolor device configuration (device B, Fig. 2B), the light emitted from the polarized PL layers is switched. This device is similar to device A but includes two polarized PL layers whose polarization directions are perpendicular to each other. We used PL layers based on EHO-OPPE and MEH-PPV that emit yellow-green and orange-red light, respectively. The switching between the "on" and "off" states changes from one bright color to another (Fig. 3C).

In device C (Fig. 2C), the excitation light is switched, and the polarized PL layer is positioned between the EO light valve and the viewer, thus functioning as an analyzer. In this case, the polarizer as well as the EO light valve must be active at the excitation wavelength. Maximum contrast now is obtained when the polarized PL layer is characterized by a high dichroic ratio for absorption and the LC cell is optimized for a single wavelength regime (for example, the UV). In this arrangement, the viewing angle is determined by the emission of the polarized PL layer, which is less angle-dependent than are LC effects. Switching of this device changed the brightness from 8 to 4 cd m^{-2}. The limited contrast and absolute brightness of the "on" and "off" states relative to those of devices A and B are attributable to the limited transparency of the commercial UV sheet polarizer that was used (about 22% at 365 nm) and, of course, the slightly lower dichroic ratio (15) of the polarized PL layer in absorption relative to emission (22). A clearly improved viewing angle was observed when comparing device C (>170°) with devices A and B (<130°).

Many other device configurations based on polarized PL layers can be envisioned, such as reflective-mode direct-view displays in which ambient light functions as the light source, pixilated multicolor structures, or stacks of multiple EO light valves and polarized PL layers (*15*). Although TN LC cells were used for all devices described above, the present concepts equally apply to displays based on alternative systems, such as electrically controlled birefringence or supertwisted nematic effect LC cells. Although green light– and orange-red light–emitting PL display devices have been demonstrated in this work, other colors (such as blue) can also be readily produced, because suitable conjugated polymers covering the full visible range are available (*2*). The technology of devices of this type, in which light emitted from the PL layer is switched, is widely compatible with commercially used backlit displays and might readily be adapted. In contrast, polarizers and LC cells of improved stability and transparency are required for the technological use of devices in which excitation light is switched.

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13. Blend films were prepared by casting a solution of the PPE (10 mg) and UHMW-PE (Hostalen Gur 412, Hoechst, 0.5 g) in xylene (50 ml) (dissolution at 130°C, after degassing the mixture in vacuum at 25°C for 15 min) into a petri dish 11 cm in diameter. The resulting gels were dried under ambient conditions for 24 hours to yield films of a homogeneous thickness of about 70 μm. These blend films were drawn at temperatures of 90° to 120°C to a draw ratio λ (final length/initial length) of about 80, to produce oriented PL layers of a thickness of about 2 μm. The PL layers were sandwiched between two glass or quartz slides; a thin layer of silicon oil fluid was applied to minimize light scattering at the film surfaces. Further details on the preparation of polarized PL layers are given in (*12*).
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A Rare-Earth Phosphor Containing One-Dimensional Chains Identified Through Combinatorial Methods

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An unusual luminescent inorganic oxide, Sr$_2$CeO$_4$, was identified by parallel screening techniques from within a combinatorial library of more than 25,000 members prepared by automated thin-film synthesis. A bulk sample of single-phase Sr$_2$CeO$_4$ was prepared, and its structure, determined from powder x-ray diffraction data, reveals one-dimensional chains of edge-sharing CeO$_6$ octahedra, with two terminal oxygen atoms per cerium center, that are isolated from one another by Sr^{2+} cations. The emission maximum at 485 nanometers appears blue-white and has a quantum yield of 0.48 ± 0.02. The excited-state lifetime, electron spin resonance, magnetic susceptibility, and structural data all suggest that luminescence originates from a ligand-to-metal Ce^{4+} charge transfer.

Combinatorial material synthesis allows large libraries to be prepared for systematic study and identification of promising lead materials. Initial studies of inorganic materials already suggest that for superconducting (*1*), magnetoresistive (*2*), and photoluminescent (*3*) solids combinatorial techniques can identify materials with superior properties among numerous similar congeners. To date, however, these studies have focused primarily on the synthesis of compositional variants, often with relatively shallow variable gradations, to optimize known properties within classes of materials with previously known structure types. We have prepared and characterized a fundamentally new type of luminescent material, Sr$_2$CeO$_4$, in which only combinatorial techniques were used to determine the elemental composition. Subsequent studies, after preparation of bulk samples of this lead composition, showed it to possess an unusual one-dimensional chain structure type, not previously seen for a luminescent rare-earth–based oxide, that is intimately related to the charge transfer mechanism by which Sr$_2$CeO$_4$ luminesces.

The luminescent phase Sr$_2$CeO$_4$ was identified by automated high-throughput screening techniques from within a discovery library of over 25,000 compositionally independent elements that was prepared by electron beam evaporation with multiple targets and moving masks (*3*). Screening for candidate materials was performed using a charge-coupled device (CCD) camera, as previously described (*3*). Comparison of the visible emission of a subsection of the library under 254-nm excitation (Fig. 1) with that of known luminescent materials identified the blue-white emission from the Sr-, Sn-, and Ce-containing region (upper right corner) as a potentially new phosphor material. A subsequent ternary focus library containing combinations of these three elements revealed that Sn was not needed for

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