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by

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Light emitting electroluminescent devices have been studied in which the conjugated light emitting polymer is separated on both sides from the device electrodes by a film of non-conducting polyaniline. The devices operate under an AC applied potential. Aluminum, copper, or gold serve as the metal electrodes. Flexible, completely organic polymer dispersed liquid crystal light valves have been fabricated from transparent plastic substrates on which a conducting film of polypyrrole has been deposited. A new concept, "microcontact printing", is being investigated for patterning the polypyrrole.

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# Application of Thin Films of Conjugated Polymers in Novel LED's and Liquid Crystal "Light Valves"

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## Abstract

Light emitting electroluminescent devices have been studied in which the conjugated light emitting polymer is separated on both sides from the device electrodes by a film of non-conducting polyaniline. The devices operate under an AC applied potential Aluminum, copper or gold serve as the metal electrodes. Flexible, completely organic polymer dispersed liquid crystal light valves have been fabricated from transparent plastic substrates on which a conducting film of polypyrrole has been deposited. A new concept, "microcontact printing", is being investigated for patterning the polypyrrole.

## Introduction

The ability to cast or deposit high quality thin films of conjugated organic polymers has permitted their use both in their lowly conducting and also in their highly conducting forms in novel electronic devices. This report describes their use in electroluminescent devices and in "all-organic" flexible light valves.

## Symmetrically Configured AC Light-Emitting (SCALE) Devices

Light emitting "5-layer" devices having the configuration M/EB/P/EB/ITO when M=Al, Cu or Au, EB=polyaniline (emeraldine base), P=poly(2,5-dihexadecanoxy phenylene vinylene pyridyl vinylene), PPV.PPyV and ITO=indium tin oxide glass show electroluminescent properties in both forward and reverse bias modes[1] (Figures 1-3). Furthermore, as shown in Figure 2, the devices can operate with an AC applied potential; two light pulses are observed in each cycle. At appropriately selected potentials, light emission in the forward bias mode is more intense when M=Al but is more intense in the reverse bias mode when M=Au. When M=Cu the intensities in the forward and reverse bias modes are approximately the same at ±~27 V. In the absence of the insulating emeraldine base, in the case of aluminum and copper, electroluminescence is observed only in the forward bias mode; in the case of gold no electroluminescence is observed in either forward or reverse bias modes.

In order to understand the role of EB, the following devices involving only aluminum were constructed in which the position and the number of layers of EB were varied from zero to one to two, viz., "3-layers":

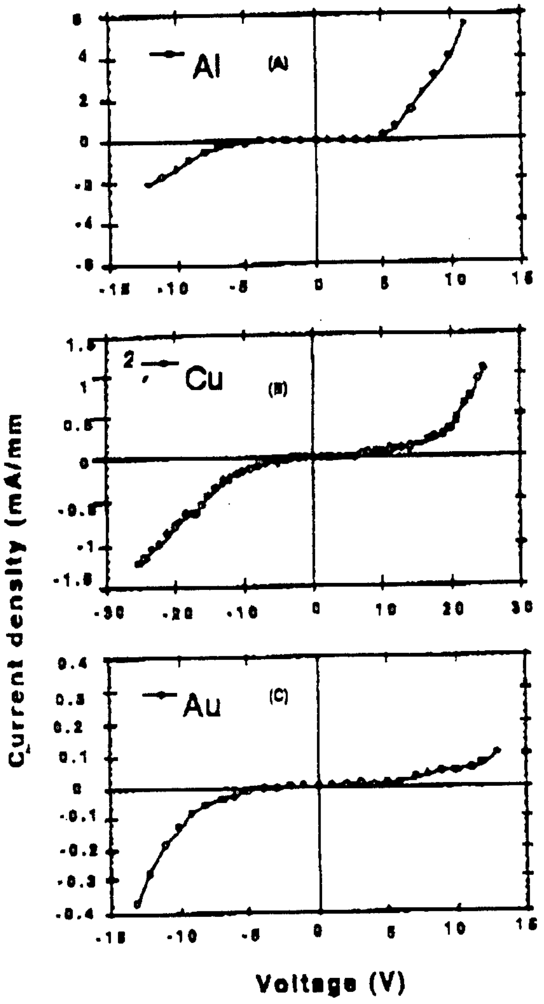

*Figure 1. I-V characteristics of SCALE devices using (A) Al (B) Cu and (C) Au, as the metal electrode.*

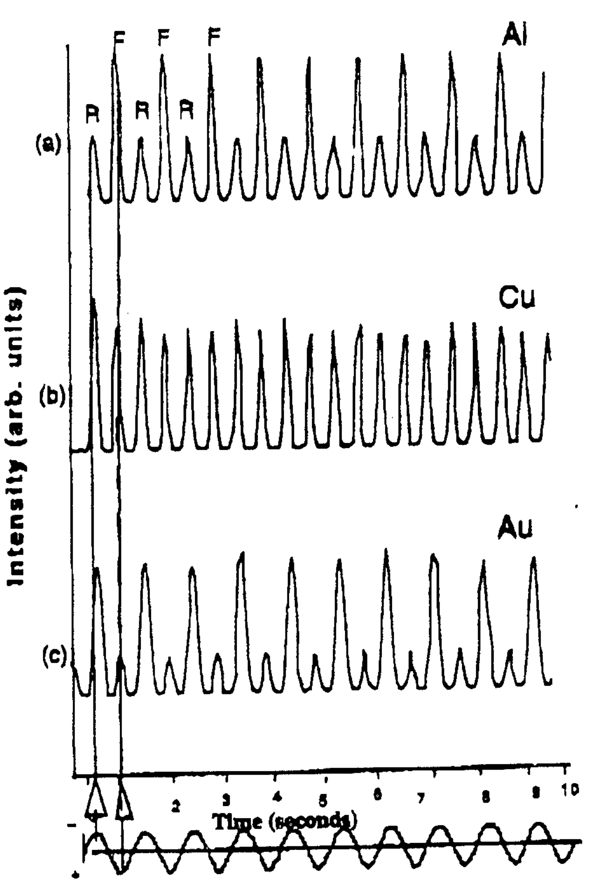

*Figure 2. Electroluminesence intensity as a function of time for a metal/EB/PPV.PPyV/EB/ITO device driven by a 1 Hz sinusoidal voltage: metal (a) Al from ±8V, (b) Cu from ±27V and (c) Au from ±8.*

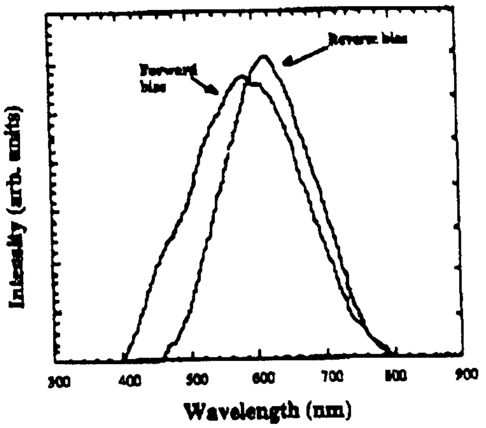

*Figure 3. Electroluminescent spectra of a Au/EB/PPV.PPyV/EB/ITO device in forward and reverse bias modes at ~±8V. For clarity, the intensity in the forward bias mode (λmax = 585nm) has been normalized to approximately the same intensity as in the reverse bias mode (λmax = 616 nm).*

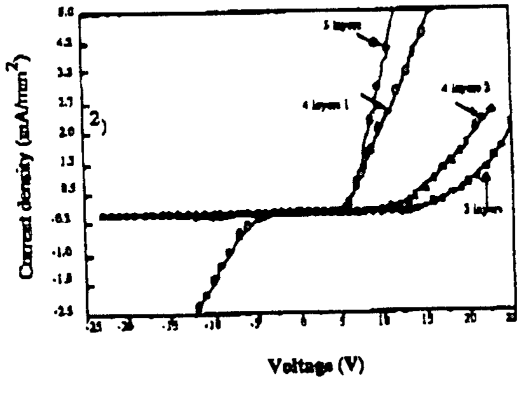

*Figure 4. I-V characteristics of 3-layered, 4-layered and 5-layered devices.*

VAl/PPV.PPyV/ITO; "4-layers-1": Al/PPV.PPyV/EB/ITO; "4-layers-2": Al/EB/PPV.PPyV/ITO; "5-layers": Al/EB/PPV.PPyV/EB/ITO. The corresponding I/V curves are given in Figure 4. Only the SCALE ("5-layers") device shows the capability of operating in both forward and reverse bias modes and in an AC mode. In the "5-layers" device only, both holes and electrons can be injected from both ITO glass and from Al electrodes. A similar phenomenon is observed when copper is used instead of aluminum in analogous "3-layers" and "5-layers" devices. As can be seen, these devices exhibit most unusual electrical properties, viz., as the number of insulating layers *increases*, the total resistance of the device at a given potential *decreases*.

Unless the electrical properties of light emitting devices are first understood it seems most unlikely that their electroluminescent properties, which are dependent on the electrical properties, can be completely understood. The possibility must be considered that under appropriate conditions, EB might act both as a good electron and as a good hole transporting material. It may be concluded that reduction in injection barriers for electrons or holes may possibly be optimized by judicious matching of electrode material which interacts chemically in a favorable manner with the polymer with which it is in contact and that the nature of the polymer/polymer interface may also play a critical role.

Preliminary studies of novel polymer light-emitting electrochemical cells[2] having a configuration such as Al/MEH-PPV+TBATS/ITO where MEH-PPV=poly(2-methoxy-5-(2'-ethyl-hexoxy)-1,4-phenylene-vinylene) and TBATS=tetrabutylammonium p-toluenesulfonate (Figure 5) show that light emission occurs in the microampere range rather than in the milliampere range as found in all other devices discussed above and that its intensity is at least an order of magnitude greater.

## Flexible Liquid Crystal Light Valves

Novel, flexible, completely organic, liquid crystal "light valves" have been fabricated using thin films of conducting polymer on flexible transparent substrates for both electrodes. Polymer Dispersed Liquid Crystal (PDLC) devices were fabricated using two flat pieces of commercial overhead transparency substrates (Nashua *xf-20*) coated with conducting polymer between which a film of commercial PDLC material (Norland Products Co. NOA 65 optical adhesive and BDH Ltd. E7 liquid crystal fluid together with EM. Ind. 15 micron polystyrene spacers) was sandwiched. The optical adhesive was polymerized by exposure to UV light.

Thin conducting films of varying controllable thickness of polypyrrole were deposited by an *in-situ* "1-dip" process on glass or flexible transparent substrates immersed in a very dilute aqueous solution of pyrrole (0.04 M) as it was undergoing oxidative polymerization at room temperature[3]. Iron(III) chloride was used as the oxidant and anthraquinone-2-sulfonate as the dopant ion.

For use in flat screen liquid crystal displays it is necessary to optimize the thickness of the polypyrrole deposit so as to simultaneously obtain the maximum transmittance and minimum resistance necessary for satisfactory devices. For example, a 10 minute dip of Nashua *xf-20* overhead transparency in the above solution produces a polypyrrole film having a thickness of ~250 angstroms, a surface resistivity of 7,200 ohms/square and a transmittance centered near the middle (600 nm) of the visible region (~400 nm to ~800 nm) of 89% using an uncoated substrate in the reference beam of the spectrometer. Figure 6 illustrates preliminary results obtained to date with a completely flexible, all organic light valve using polypyrrole as the conducting medium for both electrodes. A PDLC device using conducting ITO glass for both electrodes was used as a standard for comparison. The results are satisfactory for certain applications such as light-weight, non-breakable windows of variable transmittance. Ongoing studies with polypyrrole and poly[(3,4-ethylenedioxy)thiophene] indicate even better performance characteristics.

We are applying a new approach—microcontact printing (μCP)[4] to pattern the above liquid crystal display devices. Microcontact printing is a convenient technique for generating patterned self-assembled monolayers (SAMs) of alkanethiolates on gold and silver, and of alkylsiloxanes on hydroxyl-terminated substrates[5]. In carrying out microcontact printing on hydroxyl-terminated surfaces (for example, glass, Si/SiO$_2$, and plasma-modified polymers), an elastomeric stamp is fabricated by casting polydimethylsiloxane (PDMS) against a master (usually prepared using photolithography or micromachining, or from available relief structures such as diffraction gratings) that provides a pattern complementary to that to be reproduced. The stamp is "inked" with a solution of $C_{18}H_{37}SiCl_3$ in hexane, the solvent evaporated, and the stamp brought into contact with the surface for 5 seconds. Patterned SAMs of siloxanes with dimensions larger than 1 um can be produced routinely using this technique.

The patterned SAMs of octadecylsiloxane on these surfaces define and direct the selective deposition of polypyrrole. Immersion in an aqueous solution of polymerizing pyrrole of the type described above for ~15 minutes produced a well-defined "positive" pattern. The smallest polypyrrole features we have produced so far have ~20-30 um dimensions. Polymerization of pyrrole and deposition of the polypyrrole occurs more rapidly on the octadecylsiloxane (hydrophobic) surfaces than on the bare (hydrophilic) surfaces. Longer immersion results in losing selectivity and polypyrrole covers the entire surface. Since adhesion of polypyrrole to the hydrophobic octadecylsiloxane surfaces was found to be considerably weaker than to the hydrophilic surfaces, the polypyrrole on the hydrophobic surfaces could be readily removed by adhesive tape to form a well defined "positive" pattern on the adhesive tape, resulting in a "negative" pattern on the surface of the substrate.

The above results not only demonstrate the remarkable versatility of the new method of imaging but also highlight the importance of: (i) the nature of the substrate surface on the rate of deposition of a conducting polymer such as polypyrrole and (ii) the differing nature of the interactions

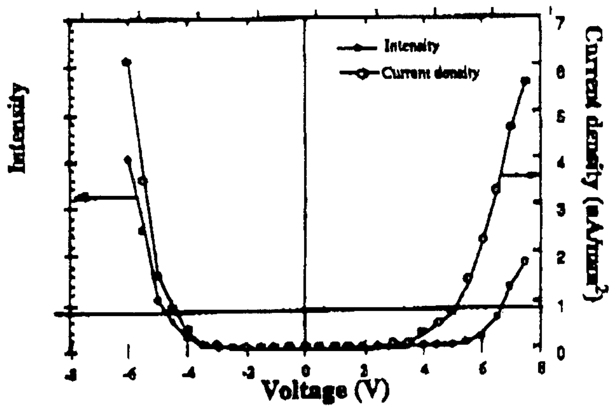

*Figure 5. Current density and intensity of light emission vs voltage in a Al/MEH-PPV+TBATS/ITO device.*

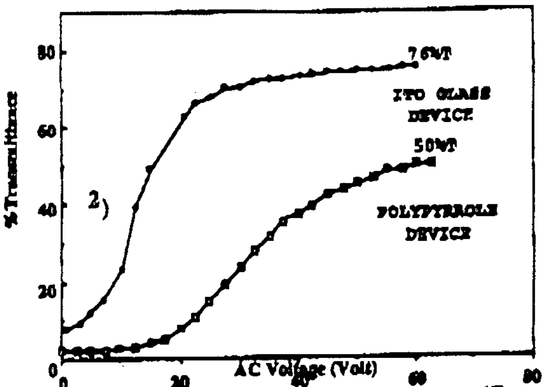

*Figure 6. Relationship between transparency (% transmittance in air at 600 nm) and applied voltage, of polymer dispersed liquid crystal display devices constructed using (A), ITO glass and (B), polypyrrole film (on plastic) as the conducting transparent substrate.*

between the as-formed polymer and the substrate as evidenced by the adhesion studies.

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# Organic Microcavities: From Light Emitting Diodes to Photopumped Lasers

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A variety of interesting and useful phenomena result when electroluminescent organic and polymeric materials are ensconced within a Fabry-Perot cavity. Such materials typically have a broad free space emission spectrum covering, in some cases, much of the entire visible wavelength range. This allows us to realize emission at the three primary color wavelengths with a single material by varying the microcavity resonance wavelength, which depends on the total optical thickness of the cavity. In our scheme we accomplish this by controlling the thickness of a single layer which is easily patternable, and is located between the organic layers and transparent contact layer. With multimode cavities it is possible to obtain mixed color (such as white) LEDs. The design rules to realize optimum devices will be described along with a description of the important optical phenomena responsible for these interesting effects. In par-