We have also measured the flow of magnetization across a twin. It is known from magnetic decoration[9], and measurements of transport[10], magnetization[11] and torque[12], that in this direction the twins act as strong pinning sites, at least at high temperatures. Our experiments at lower temperatures confirm this. In cases where the magnetization in the bulk would like to flow perpendicular to the twin, we find that magnetization piles up at the twin. The twin boundary acts as a barrier to the flow.

Given that the twins act like conduits for the flow of magnetization into the interior of the sample but block the flow across the twins, our results suggest that bulk measurements are likely to be dominated by the twins both parallel to and perpendicular to the flow of the magnetization. This suggests the need for caution in interpreting such data as measuring the intrinsic magnetic response of the YBCO system. This observation is also relevant to the issue of critical currents in these materials. When a current flows in a superconductor, energy is dissipated only if the flux lines are able to move. How and where they pin is technologically important. We expect that spatially resolved techniques capable of monitoring the dynamics will help us to understand vortex liquids, solids and glasses, and how to pin them to obtain the highest critical currents[13]. □

Received 6 April; accepted 15 May 1992.

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ACKNOWLEDGEMENTS. The work of J.P.R. and D.M.G. was supported by the NSF.

Flexible light-emitting diodes made from soluble conducting polymers

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THE recent fabrication of light-emitting diodes (LEDs) from conjugated polymers[1,2] demonstrates the technological potential of this class of electronic materials. A variety of colours are possible, because the wavelength of luminescence emission can be chemically tuned during synthesis[1–4]. In addition, the mechanical properties of polymers suggest that light-emitting structures can be made that are more flexible than their inorganic counterparts, provided appropriate materials can be found for the substrate and electrodes. Here we report the fabrication of a fully flexible LED using poly(ethylene terephthalate) as the substrate, soluble polyaniline as the hole-injecting electrode, a substituted poly(1,4-phenylene-vinylene) as the electroluminescent layer and calcium as the electron-injecting top contract. The structure is mechanically robust and may be sharply bent without failure. The LED is easily visible under room lighting and has an external quantum efficiency of about 1%. With a turn-on voltage for light emission of 2–3 V, the 'plastic' LED demonstrates that this unique combination of optical, electrical and mechanical properties can be used to make novel structures that are compatible with conventional devices.

An important advantage of the polymer LED over other electroluminescent devices is its ease of fabrication. Because the conjugated polymer active layer (or its precursor polymer) is soluble and can be deposited on a substrate from solution, simple processing techniques such as spin-casting or dipcoating can be used. The ability to apply the active luminescent polymer layer from solution makes it possible to fabricate large-area devices on flexible substrates.

In previously reported electroluminescent devices[1–4] made from organic materials (with either organic molecules or conjugated polymers as the luminescent species), the light-emitting structures were not, in fact, mechanically flexible because the injecting contacts or the substrate (or both) used brittle materials. The most widely used transparent electrode material is indium/tin oxide , but as this is brittle, the electrode is easily shattered, losing both conductivity and optical clarity.

To avoid these problems, it would be desirable to use a conducting polymer which has been doped to the metallic state to yield a highly conducting and transparent thin film on a polymer substrate. Although transparent conducting polymer electrodes have been reported[5–7], they are polymerized *in situ*, in a matrix polymer or on the surface of a polymer substrate. Such processes are necessarily slow. Furthermore, they typically require a catalyst or an oxidizing agent, which affects the purity of the active semiconducting layer and the efficiency of the device.

Figure 1 shows schematically the structure of the flexible 'plastic' light-emitting diode. The device consists of a free-standing poly(ethylene terephthalate) (PET) film as substrate, a thin film of polyaniline (PANI) as the hole-injecting contact, a film of poly(2-methoxy, 5-(2′-ethyl-hexoxy)-1,4-phenylene-vinylene) (MEH-PPV) as the active electroluminescent layer, and a calcium electrode as the metallic electron-injecting contact.

Polyaniline films were spin-cast from solution in the conducting form (emeraldine salt) onto the PET substrate. Before use, the PET film (thickness 100 μm) was cleaned by boiling first in acetone and then isopropanol, and dried at 80 °C for 1 hour. The PANI solution was prepared using the method of ref. 8 which uses functionalized protonic acid solutes to dope polyaniline and render the resulting PANI complex soluble in common organic solvents. In such complexes[8], the counter-ion, (M^--R), contains the R functional group which is chosen to be compatible with nonpolar or weakly polar organic liquids.

An example of a transparent electrode for the flexible LED structure is camphor sulphonic acid (CSA) as the R functional group. After doping and complexation with CSA, the conducting PANI-complex is soluble in *m*-cresol and can be spin-cast onto

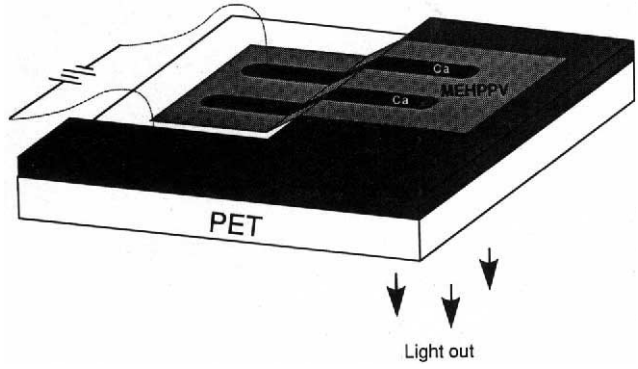

FIG. 1 Schematic diagram of the structure of a flexible light-emitting diode. The device is built on a PET substrate with successive layers as follows: PANI, then MEH-PPV, then Ca (see text). Film thicknesses are as follows: PANI-CSA, ~0.5 μm; MEH-PPV, 1,000–1,500 Å; calcium, <1,000 Å.

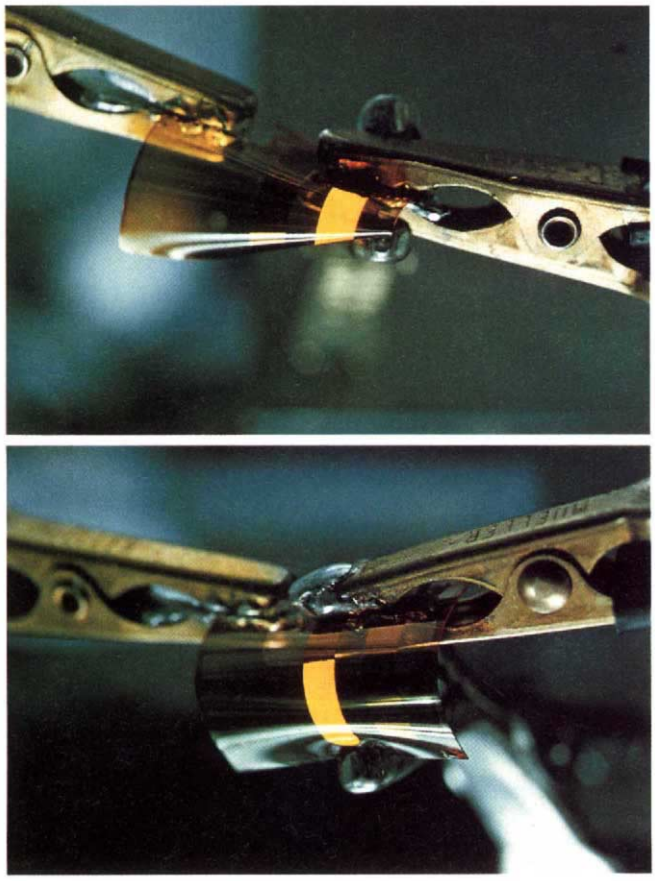

FIG. 2 Photographs of the flexible light-emitting diode at an applied bias voltage (positive on the PANI electrode) of 6 V. The structure of the device is shown in Fig. 1.

a variety of substrates, including glass and PET, to make optical-quality transparent films with low surface resistance[9]. Such films can achieve surface resistances lower than 100 Ω per square while retaining transmission greater than 70% at visible wavelengths greater than 475 nm (green to red)[9].

The PANI-CSA films used for the hole-injecting contacts were spun from solution in meta-cresol (4% by weight) and dried at 60 °C for 12 hours. The thickness and accordingly the surface resistance of the PANI electrode are controlled by varying the spinning speed and/or the concentration of the PANI solution[9]; the films used in the flexible LEDs had a surface resistance of ~200 Ω per square.

Contact to the PANI electrode was made by a thin, vacuum-evaporated gold film. Although we used gold initially to make certain that the PANI electrode was not current-limiting, we find that excellent ohmic contacts are made to the transparent PANI electrode with silver paste or, simply, with an alligator clip. A layer of MEH-PPV[10] was deposited on the PANI surface by spin-casting from solution of MEH-PPV in xylene (0.5 wt%). We saw no indication of dissolution of the PANI by the MEH-PPV solution. The two-component system was designed so that each component, the PANI-CSA complex and MEH-PPV, was separately soluble, but each was insoluble in the solvent that dissolved the other. The deposition of the MEH-PPV layer was carried out in nitrogen atmosphere in a controlled-atmosphere dry-box.

The calcium electron-injecting contact[2] was deposited by vacuum evaporation at a pressure below 10^{-6} torr. Because calcium oxidizes rapidly in air, the evaporator was mounted inside the dry box, and all physical measurements were carried out with the LEDs in the dry box. The electrode was initially passivated by over-coating with aluminium and then applying a protective polymer layer (with such protection, slow degradation occurs in air over a period of weeks).

Two flexible LEDs (under forward bias at 6 V) are shown in Fig. 2 with alligator clips used as contacts. The photographs are taken through the transparent PANI electrode; the calcium back-electrode serves as a mirror that reflects part of the emitted light. The light emitted by the device is visible under ordinary room lighting even at low bias voltages. As pure MEH-PPV is a high-resistivity semiconductor (bandgap ~2.1 eV), the emitting area is defined by the calcium contact. Patterning of the flexible devices is easily accomplished by masking during the evaporation. As the figure shows, the 'plastic' LED is flexible and can be curled and bent repeatedly (even folded back on itself in a sharp 180° bend) without failing or losing surface conductance, in contrast to indium/tin oxide-coated PET. The robust nature of the four-layer structure clearly proves the excellent mechanical adhesion of the PANI/MEH-PPV and PANI/PET contact (and, in addition, of the Ca/MED-PEV contact).

The PANI electrode has a light green colour, as it has a transmission window extending from ~475 nm. The absorption spectrum of the PANI electrode (Fig. 3) shows the characteristic features of the emeraldine salt form of PANI with a strong absorption peak at 440 nm and a broad absorption band extending into the infrared. The latter has been interpreted as resulting from the free-carrier absorption from the partially filled band in a polaronic metal[11]. As can be seen from the spectrum in Fig. 3, the electroluminescence from the semiconducting MEH-PPV active layer falls right in the transmission window between the two principal absorptions of the PANI electrode.

Figure 4 shows the current-voltage (I-V) characteristic of a

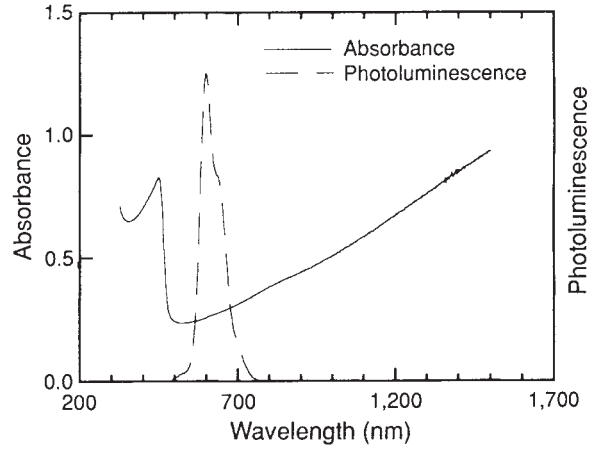

FIG. 3 The absorption spectrum of a PANI-CSA film compared with the photoluminescence spectrum of a MEH-PPV film.

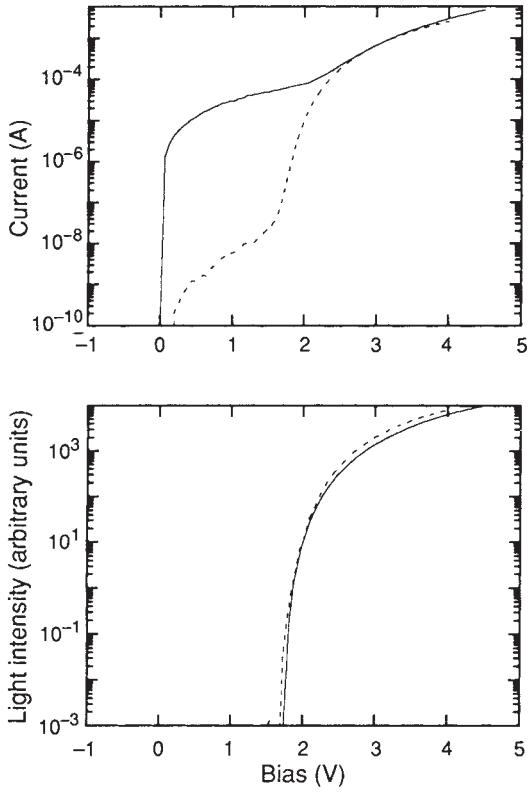

FIG. 4 The current (top) and electroluminescent intensity (bottom) as a function of applied bias voltage for light-emitting diodes with glass/ITO (- - - -) and PET/PANI (——) hole-injecting electrodes. The two devices have equal areas, 0.1 cm^2.

flexible LED device, together with that of a device using indium/tin oxide (ITO) as the hole-injecting contact. At low bias (<1.8 V), the current is 10^3–10^4 times higher in the PANI/MEH-PPV/Ca device than in the ITO/MEH-PPV/Ca device. Above 1.8 V, however, in the range where the devices start to emit light, the currents through the two devices are similar. The luminescence intensities of the two devices (PANI or ITO electrode) are nearly identical; the quantum efficiencies (photons per electron) are ~1%.

Because the characteristics of the indium/tin oxide and the PANI devices are similar at high voltages, the two transparent electrode materials have similar hole-injecting properties. This can be rationalized by comparing their work functions. The work function of PANI as measured by photoelectron spectroscopy is 4.3 eV (P. Dannetun, personal communication), close to that of indium/tin oxide which has been reported[12] as 4.1 eV. We note, however, that the chemical stoichiometry and morphology of indium/tin oxide (and thus the work function) vary when such electrodes from different sources are compared. □

Received 14 February; accepted 16 April 1992.

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Preparation and characterization of $C_{60}Br_6$ and $C_{60}Br_8$

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BUCKMINSTERFULLERENE (C_{60}) is much more reactive than was originally anticipated, because resonance structures that place double bonds in the pentagonal rings are energetically unfavourable[1] and lead to restricted electron delocalization. C_{60} therefore behaves as an electron-deficient 'super-alkene' rather than as a 'super-aromatic', as demonstrated by the addition of osmium tetroxide[2], platinum[3], dipolar molecules[4], alkyl radicals[5] and amines[6]. Reaction of anions derived from C_{60} with iodomethane results in up to 24 methyl groups becoming attached to the cage, although compounds containing either eight or six methyl groups are dominant in the mass spectrum[7]. Here we report the synthesis of crystalline $C_{60}Br_6$ (which forms magenta plates) and $C_{60}Br_8$ (dark brown prisms) by mixing solutions of C_{60} with bromine. The structures of these compounds, which contain occluded bromine when precipitated from the brominating medium, have been determined by single-crystal X-ray diffraction. Reaction of C_{60} with bromine in the absence of solvent gives $C_{60}Br_{24}$ (which also contains occluded bromine). We propose a configuration for $C_{60}Br_{24}$ (and sterically hindered $C_{60}X_{24}$ compounds) based on that for $C_{60}Br_8$. On being warmed in solution, $C_{60}Br_6$ rearranges and disproportionates to $C_{60}Br_8$, and all three bromo derivatives revert to C_{60} on strong heating. These results provide an insight into the pattern of addition of bulky reagents to C_{60}.

Halogeno compounds are important synthetic intermediates, being reactive towards many nucleophiles[8]. Halogenation of

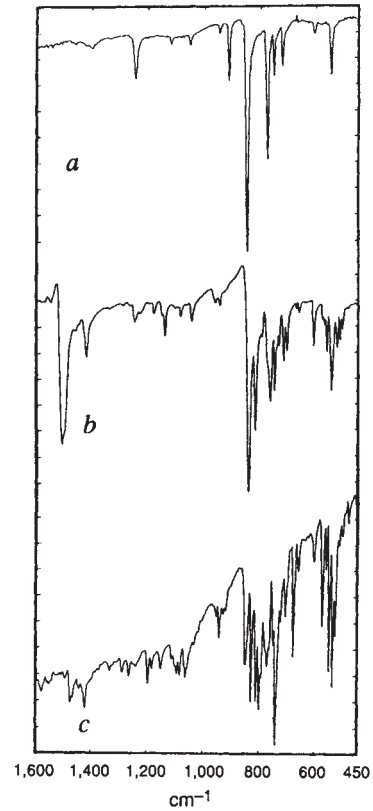

FIG. 1 Infrared spectra of (*a*) $C_{60}Br_{24}$; (*b*) $C_{60}Br_8$; (*c*) $C_{60}Br_6$. The strong C=S stretching band in spectrum *b* is due to occluded CS_2.