chromated Mo Kα radiation (52 kV, 110 mA). 2282 reflections were collected in the range $2° \leq \theta \leq 28°$, which gave 1644 symmetry-independent reflections with $I \geq 2\sigma(I)$ used, after absorption correction based on empirical ψ scan ($\mu = 0.634$ mm^{-1}), in the structure solution (direct methods: SHELX-86) and least-squares refinement (SHELX-93) of 104 parameters. All non-hydrogen atoms were refined anisotropically, and H atoms, located in ΔF maps, isotropically (with one common temperature factor). Final R and wR_2 values were 0.0431 and 0.1417, respectively. Further details of the crystal structure determination are available on request from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK, on quoting the names of the authors and the journal citation.

Received: September 9, 1997
Final version: November 17, 1997

---

[1] J. W. Sease, L. Zechmeister, *J. Am. Chem. Soc.* **1947**, *69*, 270. L. Zechmeister, J. W. Sease, *J. Am. Chem. Soc.* **1947**, *69*, 273.
[2] G. Horowitz, D. Fichou, X. Z. Peng, Z. G. Xu, F. Garnier, *Solid State Commun.* **1989**, *72*, 381.
[3] A. Dodabalapur, L. Torsi, H. E. Katz, *Science* **1995**, *268*, 270.
[4] G. J. Visser, G. J. Heeres, J. Wolters, A. Vos, *Acta Crystallogr., Sect. B* **1968**, *24*, 467.
[5] P. A. Chaloner, S. R. Gunatunga, P. B. Hitchcock, *Acta Crystallogr., Sect. C* **1994**, *50*, 1941.
[6] M. Pelletier, F. Brisse, *Acta Crystallogr., Sect. C* **1994**, *50*, 1942.
[7] F. Van Bolhuis, H. Wynberg, E. E. Havinga, E. F. Meijer, E. G. J. Staring, *Synth. Met.* **1989**, *30*, 381.
[8] B. Servet, S. Ries, M. Trotel, P. Alnot, G. Horowitz, F. Garnier, *Adv. Mater.* **1993**, *5*, 461.
[9] W. Porzio, S. Destri, M. Mascherpa, S. Rossini, S. Bruckner, *Synth. Met.* **1993**, *55*, 408.
[10] G. Horowitz, B. Bachet, A. Yassar, P. Lang, F. Demanze, J. L. Fave, F. Garnier, *Chem. Mater.* **1995**, *7*, 1337.
[11] D. Fichou, B. Bachet, F. Demanze, I. Billy, G. Horowitz, F. Garnier, *Adv. Mater.* **1996**, *8*, 500.
[12] T. Siegrist, R. M. Fleming, R. C. Haddon, R. A. Laudise, A. J. Lovinger, H. E. Katz, P. Bridenbaugh, D. D. Davis, *J. Mater. Res.* **1995**, *10*, 2170.
[13] R. Hajlaoui, G. Horowitz, F. Garnier, A. Arce-Brouchet, L. Laigre, A. El Kassmi, F. Demanze, F. Kouki, *Adv. Mater.* **1997**, *9*, 389.
[14] A. J. Lovinger, D. D. Davis, A. Dodabalapur, H. E. Katz, *Chem. Mater.* **1996**, *8*, 2836.
[15] D. R. Ferro, W. Porzio, S. Destri, M. Ragazzi, S. Brückner, *Macromol. Theory Simul.* **1997**, *6*, 713.

Polymer Light-Emitting Electrochemical Cells with Frozen p-i-n Junction at Room Temperature**

By *Gang Yu*, *Yong Cao*, *Mats Andersson*, *Jun Gao*, and *Alan J. Heeger**

The light-emitting electrochemical cell (LEC)[1,2] provides a novel approach to achieving light emission from semiconducting (luminescent) polymers. Experimental and theoretical studies of LECs have focused on elucidating the operating mechanism and on improving device performance.[3–14]

Conventional metal/polymer/metal light-emitting diodes (LEDs) are dual carrier devices in which electrons and holes are injected at the cathode and anode, respectively, into the undoped semiconducting polymer.[15] To minimize the potential barriers at the polymer/metal interfaces and to optimize carrier injection, the cathode and the anode should be chosen with work functions matching the bottom of the conduction band (π^*) and the top of the valance band (π) of the semiconducting polymer, respectively. It is difficult, therefore, to satisfy the conditions required for efficient, balanced injection for polymers with different bandgaps and with different ionization potentials.

Polymer LECs avoid this problem by utilizing a polymer blend containing semiconducting luminescent polymer and solid-state electrolyte.[1,2] As a result of electrochemical redox doping and the associated redistribution of the ions in the solid electrolyte, a p-i-n junction is created in situ by applying a voltage greater than the energy gap of the semiconducting polymer. The p- and n-type doped regions provide ohmic contacts for balanced charge injection; light emission occurs in the insulating (i) region in between. Electrochemical doping and the formation of a p-i-n junction (with built-in potential) were confirmed by optical beam induced current (OBIC) experiments.[10]

LECs demonstrated previously were operated in the dynamic-junction mode at room temperature (RT); the junction forms and decays dynamically with the external bias.[2–11] Since the ions move and the junction changes un-

---

[*] Prof. A. J. Heeger, Dr. G. Yu, Dr. Y. Cao, Dr. M. Andersson[+]
UNIAX Corporation
6780 Cortona Drive, Santa Barbara, CA 93117-3022 (USA)

Prof. A. J. Heeger, Dr. M. Andersson,[+] Dr. J. Gao
Institute for Polymers and Organic Solids
University of California at Santa Barbara
Santa Barbara, CA 93106-5090 (USA)

[+] Current address: Dept. of Organic Chemistry and Polymer Technology, Chalmers University of Technology, S-41296 Goteborg, Sweden.

[**] We are grateful to Dr. Q. Pei, Dr. C. Zhang, and Dr. I. D. Parker for comments and discussions. The work at UNIAX was partially supported by the Office of Naval Research under the DOD SBIR program (N00014-96-C-0406); work at UCSB was supported by the National Science Foundation under Grant No. ECE-9528204.

der external bias, these LECs show slower response than polymer LEDs.[2–4] Moreover, overdoping (and degradation) occurs when LECs are driven at a voltage beyond the electrochemical stability window of the luminescent polymer/electrolyte/electrode system. Gao et al.[16] demonstrated recently that the p-i-n junction in LECs containing polyethylene oxide (PEO) as the ion transport medium can be frozen at 100 K. In the frozen-junction mode, LECs can be operated with response times similar to those of polymer LEDs, but with improved and more nearly balanced injection.[16]

In this communication, we demonstrate bright polymer LECs that operate *at room temperature* in the frozen p-i-n junction mode, with performance characteristics similar to those of polymer LEDs, including unipolar *I-V* dependence, light emission in forward bias only, and fast response. Frozen-junction LECs can be operated at high bias voltages and high current densities; the luminance is over 20 000 cd/m^2 at 8 V and 550 mA/cm^2 with an external quantum efficiency of ~2.4 % ph/el (photons/electron) and a luminous efficiency ~5.6 lm/W; values that are comparable to or even better than the best green or yellow emissive devices.

The electroluminescent (EL) polymers used for this study were poly(2-butyl-5-(2-ethyl-hexyl)-1,4-phenylene vinylene) (BuEH-PPV) and poly(2,5-bis(cholestanoxy)-1,4-phenylene vinylene) (BCHA-PPV), synthesized according to published procedures.[17,18] Their molecular structures are shown in Figure 1. Both are soluble in common organic solvents such as xylene or toluene. BuLEH-PPV and BCHA-PPV emit green and yellow light, respectively; their EL spectra are shown in Figure 1. The corresponding color coordinates are (0.37, 0.58) and (0.50, 0.49), respectively, in the CIE 1931 chromaticity diagram.

The LECs were fabricated in the standard metal/LEC-blend/metal sandwich structure.[1–4] The electrochemically active blends were prepared with the luminescent polymers mixed with electrolyte containing crown ether and Li triflate, as discussed by Cao et al.[19] In some devices, the surfactant-like additive octylcyanoacetate (OCA) was added to improve the microstructure of the phase-separated blend.[4] In these experiments, the molar ratio of lithium salt to crown ether was 0.5. The molar ratio between crown ether and BuEH-PPV was varied from 1:10 to 1:1. Indium tin oxide (ITO) coated glass was used as the substrate. Optical quality, uniform films (thickness ~2000 Å) were obtained by spin-casting from xylene solution. Aluminum was used as the back metal electrode. The area of each test device was ~0.15 cm^2. Devices were characterized with a Keithley 236 source measurement unit; the emitted light intensity was measured with a calibrated Si photodiode. A pulse generator (HP 8116A) and a digital oscilloscope (Tektronix 340A) were used for transient response measurements.

Because the ionic conductivity in the crown-ether electrolyte is negligible at RT,[19] the performance of pristine devices is similar to that of conventional LEDs. The EL efficiency is ~0.04 % ph/el at low current level, comparable to that observed in polymer LEDs made in the Al/BuEH-PPV/ITO configuration. The pristine devices show relatively high device resistance as revealed through fast *I-V* scans (see Fig. 2).

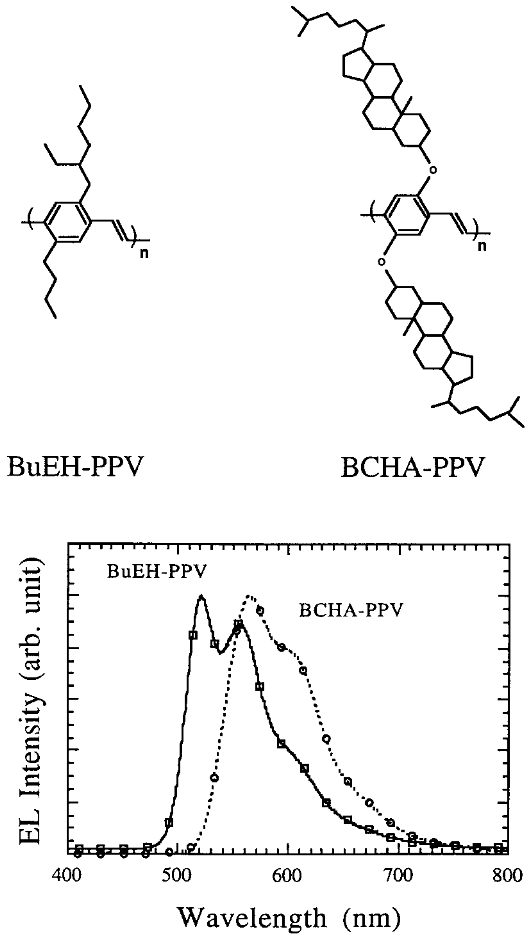

Fig. 1. Chemical structures (top) and electroluminescent spectra (bottom) of BuEH-PPV and BCHA-PPV.

Conversion to LECs was achieved by turning on the ionic conductivity at elevated temperatures with associated electrochemical redox doping near the electrodes. For example, devices could be "activated" by applying a fixed low voltage, 3–4 V, while running the device at elevated temperatures (60–80 °C). After cooling the device to RT, *I-V* scans indicated that the electrical and EL characteristics had changed dramatically. The injection current at 8 V improved by >10^3 times, with an associated increase in EL intensity. More importantly, as shown in Figure 3, electron and hole injection approached balance, as indicated by an improved quantum efficiency from ~0.04 % ph/el to 2.5 % ph/el.

Junction formation was also accomplished through self-heating. For example, after repeatedly scanning the devices to the level of 0.1–0.5 A/cm^2 at slow scan rates, the operating voltage corresponding to 0.5 A/cm^2 decreased from 15–

20 V to ~8 V and stabilized. Simultaneously, a bright emission spot appeared and expanded to cover the entire device area. The surface temperature of the emitting area was measured; in the stable state at 0.4 A/cm^2 (6–8 V), the surface temperature was 60–80 °C.

A p-i-n junction was created in the LEC under bias at elevated temperatures, as indicated by the rectifying *I-V* curve shown in Figure 2. In forward bias (defined as the direction of the bias applied during junction formation at elevated temperatures), the *I-V* curve is characterized by turn-on at ~2.1 V followed by an exponential current increase, $I \sim \exp(V/V_0)$, by more than four orders of magnitude. The slope, V_0, is approximately 150 meV, which is slightly larger than that observed in high-efficiency polymer LEDs made with MEH-PPV (poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene)).[20] For $V > 3$ V, the rate of current increase becomes slower and sub-exponential. Below 2 V and in reverse bias, the current is dominated by leakage. The rectification ratio at 4 V is 10^4–10^5, comparable to that observed in high-performance polymer LEDs. Freeze-out of ionic conductivity was evident: i) no hysteresis was observed in fast *I-V* scans for $I < 0.2$ A/cm^2, ii) *I-V* scans were unipolar (rectifying), and iii) "battery" discharge current was negligible at zero bias; all in contrast to observations in polymer LECs made with PEO/Li$^+$ and operated in the dynamic-junction mode at RT.[1–4] Thus, the p-i-n junction is frozen at RT.

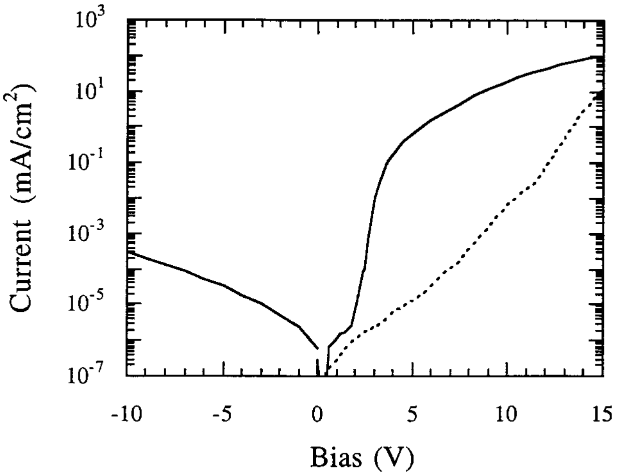

Fig. 2. *I-V* characteristics of a BuEH-PPV/CE/Li$^+$ LEC in pristine condition (dotted line) and with frozen p-i-n junction (solid line).

Green light emission was detected in the frozen-junction BuEH-PPV/CE/Li$^+$ LECs for $V > 2.1$ V, as shown in Figure 3 (CE: counter electrode). Shown in Figure 3 are data from two frozen-junction LECs with and without the surfactant OCA (denoted as D1 and D2). The weight ratios of the blends are BuEH-PPV/CE/Li triflate/OCA = 1:1:0.2:0.1 for D1 and BuEH-PPV/CE/Li triflate = 2:1:0.2 for D2. In D1, the luminance reaches ~21 400 cd/m^2 at 8 V. The corresponding external EL efficiency (η_{EL}) for the same BuEH-PPV LECs are shown in the inset of Figure 3; η_{EL} persists at 2.5 % ph/el (D1) and 3.0 % ph/el (D2) over a broad current range. In the LECs without OCA, the EL efficiency is even higher; however, the operation voltage is nearly doubled at high emission intensity. The maximum luminous efficiencies are approximately 5.6 m/W for D1 and 4.4 lm/W for D2 (at ~6 V), among the best reported for green-emitting devices, even including LEDs made with inorganic materials.

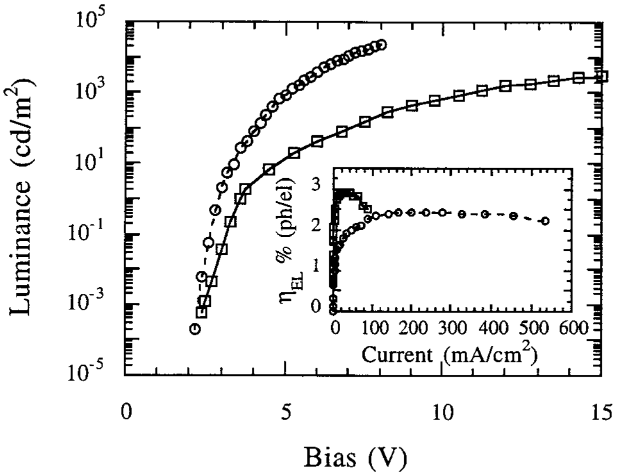

Fig. 3. *L-V* in two frozen-junction LECs with different blend ratios (circles: BuEH-PPV/CE/Li triflate/OCA = 1:1:0.2:0.1; squares: BuEH-PPV/CE/Li triflate = 2:1:0.2). Their corresponding external quantum efficiencies are shown in the inset.

Because of the freeze-out of ionic motion at RT, the external bias can be increased to values required for multiplexing without overdoping, as indicated by a flat *η-I* curve and linear *L-I* data. This is in contrast to LECs operating in dynamic mode,[2–11] in which the EL efficiency decreases for bias voltages outside the electrochemical window of stability (larger than 3–4 V in semiconducting polymers) because of degradation through overdoping.

Photovoltaic effect measurements were carried out on the frozen-junction LECs to determine the built-in potential (monochromatic light, 10 mW/cm^2 at 450 nm, was used as the excitation source). The open-circuit voltage and the short-circuit current were ~1.8 V and 0.1 µA/cm^2, respectively, for the LECs made with BuEH-PPV. The exponential current turn-on at 2.1 V with light emission for $V > 2.1$ V[5] and the open-circuit voltage of ~2 V are consistent with a p-i-n junction in the frozen-junction LECs. The built-in potential of ~2 V is consistent with the energy difference expected between the p-doped and the n-doped polaron energy levels in the semiconducting polymer.

Transient experiments were carried out for a BuEH-PPV/CE(Li$^+$) LEC with results as shown in Figure 4. The LECs were driven by a train of square wave pulses, and light-emission waveforms were recorded. The rise and fall time is in the range of 25–35 µs, in contrast to the millisecond response time typically seen in LECs in the dynamic-junction mode.[2–3] In fact, the response time of LECs in the frozen-junction mode is of the same magnitude as that

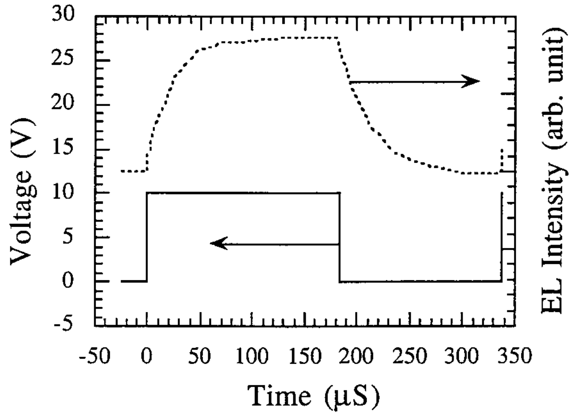

Fig. 4. Transient response of a BuEH-PPV/CE/Li$^+$ LEC.

measured in polymer LEDs in a similar configuration (single layer, same size, and similar thickness) and tested with the same photodetector. Since these response times are close to the *RC* limit of the Si photodetector, the data in Figure 4 provide only an upper limit to the intrinsic response time. The fast response implies that only electronic processes are involved, proving again that the p-i-n junction is frozen at room temperature.

Frozen-junction LECs were also fabricated with BCHA-PPV. In contrast to the relatively low efficiency and high operating voltage that characterize single-layer LEDs made with this material,[21] the BCHA-PPV/CE/Li$^+$ frozen-junction LECs show high EL efficiency. The *I-V* and *L-V* data are similar to those shown in Figure 2 with an external quantum efficiency of ~3 % ph/el at 3 V.

LECs operated in the frozen-junction mode retain all the advantages of LECs operating in the dynamic-junction mode, including optimized and balanced carrier injection, high EL efficiency, and low operating voltage. Moreover, the principal drawbacks of dynamic-junction operation are overcome, and the response speed is improved to the level of polymer LEDs. Furthermore, overdoping (which results in decreased efficiency and device degradation) is avoided by freeze-out of ionic mobility, thus enabling LECs to be driven to high brightness at voltages well outside the electrochemical window of stability.

The criteria for EL devices suitable for *x-y* addressable flat-panel display include: i) fast response time; ii) high luminance intensity, which enables multiplexing at low duty cycle; iii) unipolar, switch-like *I-V* to avoid cross-talk; and iv) full-color capability. Frozen-junction LECs fulfill all these criteria and therefore provide an attractive approach to fabricating column–row addressable, high pixel density, full-color displays.[6]

In summary, bright LECs operating in the frozen-junction mode at room temperature were fabricated by using Li salt/crown ether complexes as the solid electrolyte. The electrical and optical characteristics are similar to those of LEDs, including unipolar (rectifying) current–voltage dependence, light emission in forward bias only, and fast response. The external EL efficiency and luminous efficiency with BuEH-PPV as the EL polymer are ~2.4 % ph/el and 5.6 lm/W, respectively, values that rank among the best for EL devices with green emission. The freeze-out of ionic motion allows these LECs to be driven to high bias voltages, well beyond the electrochemical stability window of the luminescent polymer; >20 000 cd/m^2 was achieved at 8 V bias. These features make the frozen-junction LECs attractive for use in the fabrication of high pixel density, column–row addressable emissive displays.

Received: September 1, 1997

---

[1] Q. Pei, F. Klavetter, *US Patent Application 8/268 763*, **1994**.
[2] Q. Pei, G. Yu, C. Zhang, Y. Yang, A. J. Heeger, *Science* **1995**, *269*, 1086.
[3] Q. Pei, Y. Yang, G. Yu, C. Zhang, A. J. Heeger, *J. Am. Chem. Soc.* **1996**, *118*, 3922.
[4] Y. Cao, G. Yu, C. Y. Yang, A. J. Heeger, *Appl. Phys. Lett.* **1996**, *68*, 3218.
[5] G. Yu, Y. Yang, Y. Cao, Q. Pei, C. Zhang, A. J. Heeger, *Chem. Phys. Lett.* **1996**, *259*, 465.
[6] G. Yu, Q. Pei, C. Zhang, Y. Cao, Y. Yang, A. J. Heeger, presented at *MRS Spring Mtg.*, San Francisco, CA, April 8–12, **1996**.
[7] Y. Yang, Q. Pei, *J. Appl. Phys.* **1996**, *78*, 2708.
[8] Y. Yang, Q. Pei, *J. Am. Chem. Soc.* **1996**, *118*, 7416.
[9] Y. Yang, Q. Pei, *J. Appl. Phys.* **1997**, *81*, 3294.
[10] D. J. Dick, A. J. Heeger, Y. Yang, Q. Pei, *Adv. Mater.* **1996**, *8*, 985.
[11] Y. Greenwald, F. Hide, J. Gao, F. Wudl, A. J. Heeger, *J. Electrochem. Soc.* **1997**, *144*, L70.
[12] D. L. Smith, *J. Appl. Phys.* **1997**, *81*, 2867.
[13] J. Manzanares, H. Riess, A. J. Heeger, *J. Phys. Chem.*, in press.
[14] I. Riess, D. Cohen, *J. Appl. Phys.*, in press.
[15] I. D. Parker, *J. Appl. Phys.* **1994**, *75*, 1656.
[16] J. Gao, G. Yu, A. J. Heeger, *Appl. Phys. Lett.* **1997**, *71*, 1293.
[17] M. R. Andersson, G. Yu, A. J. Heeger, *Synth. Met.* **1997**, *85*, 1275.
[18] F. Wudl, S. Höger, C. Zhang, K. Pakbaz, A. J. Heeger, *Polym. Prepr.* **1993**, *34*, 197.
[19] Y. Cao, M. R. Andersson, Q. Pei, G. Yu, A. J. Heeger, unpublished.
[20] D. Braun, A. J. Heeger, *Appl. Phys. Lett.* **1991**, *58*, 1982. G. Yu, C. Zhang, A. J. Heeger, *Appl. Phys. Lett.* **1994**, *64*, 1540.
[21] C. Zhang, S. Höger, K. Pakbaz, F. Wudl, A. J. Heeger, *J. Electron. Mater.* **1993**, *22*, 413.

Photoinduced Switching in Self-Assembled Multilayers of an Azobenzene Bolaamphiphile and Polyelectrolytes

By *Farnaz Saremi* and *Bernd Tieke**

The reversible cis–trans photoisomerization of azobenzene and its derivatives has been investigated in several media.[1–4] The transition from the thermodynamically more stable trans to the cis configuration can be induced upon irradiation with UV light ($\lambda_1 < 370$ nm) and reversed upon heating or irradiation with visible light ($\lambda_2 > 430$ nm). Several studies on the photoisomerization of azobenzene derivatives in molecularly thin films such as Langmuir and

---

[*] Prof. B. Tieke, Dr. F. Saremi
Institut für Physikalische Chemie der Universität zu Köln
Luxemburgerstrasse 116, D-50939 Köln (Germany)