

DOI: 10.1002/adma.200602087

Long-Lifetime Polymer Light-Emitting Electrochemical Cells**

By Yan Shao,* Guillermo C. Bazan, and Alan J. Heeger*

Polymer light-emitting devices have been divided into two general types: polymer light-emitting diodes (PLEDs) and polymer light-emitting electrochemical cells (PLECs).^[1–5] The advantages of PLEDs include a fast response and relatively long operating lifetime (with proper packaging). However, low-work-function cathodes and/or thin interfacial layers (e.g., LiF) between the metal and the emitting polymer layer are required. In contrast, PLECs have relatively low turn-on voltages (approximately equal to the bandgap of the luminescent semiconducting polymer), and low work-function metals are not required.

One of the serious disadvantages of PLECs, however, is the slow response time (the time required for the mobile ions to diffuse during junction formation). A solution to this problem is to “freeze” the junction after ion redistribution.^[6,7] A frozen junction system that operates at room temperature is necessary for practical use. A second limiting disadvantage of PLECs has been the short operating lifetimes compared with those of PLEDs.^[8,9]

We report here the results of an initial study of light emission from a luminescent polymer blended with a dilute concentration of an ionic liquid. Even with an aluminum cathode, the devices turn on at low voltage (approximately equal to the bandgap of the luminescent semiconducting polymer). These ionic-liquid-containing LECs were operated continuously in the glove-box (without packaging) for several days without significant degradation in brightness. After sealing with epoxy and a glass cover slide, the ionic-liquid-containing LECs were operated continuously in air for several weeks.

The major difference between PLEDs and PLECs is that the latter possess mobile ions inside the polymer; therefore, the selection of the mobile ions is one of the keys to fabricating high-performance PLECs. Previously, the mobile-ion systems that have been used fall into three categories. The first is polyethylene oxide (PEO) containing Li salts.^[2,3] Crown ethers (and derivatives)^[9,10] and other organic salts^[11,12] have

also been used in combination with metal salts. Finally, polymers with ionic side chains (polyelectrolyte conjugated polymers) and appropriate mobile counterions have been used.^[13] For almost all PLECs, the additives comprise at least 5 wt %. More importantly, these systems involve two-component phase separation with the emitting polymer in one phase and the mobile ions (e.g., dissolved in PEO) in a second phase. To create the p-type–intrinsic–n-type (p-i-n) junction of the LEC, ions must move from one phase into the other; for example, from the PEO into the luminescent polymer. This phase separation appears to degrade the device performance, especially the lifetime.^[10] The phase separation results from the relatively poor compatibility of the ionic materials (hydrophilic) with the host light-emitting polymers (hydrophobic). In order to reduce the phase separation, surfactants or bifunctional additives were introduced into the emitting layer and better performance was reported.^[14] Single-component PLEC polymers have been fabricated using luminescent polymers with ionic side chains (polyelectrolyte conjugated polymers), but the electroluminescence (EL) was weak and the operating lifetimes were poor.^[13]

In the devices described here, we utilized the simplest sandwich structure for the device configuration with poly(3,4-ethylene dioxythiophene)–poly(styrene sulfonate) (PEDOT–PSS) coated indium tin oxide (ITO) glass as the anode and aluminum as the cathode. The well-known soluble phenyl-substituted poly(*para*-phenylene vinylene) (PPV) copolymer (“superyellow” from Merck/Covion)^[15] was selected as our host light-emitting polymer and an organic ionic liquid, methyltriocylammonium trifluoromethanesulfonate (MATS), was used to introduce a dilute concentration of mobile ions into the emitting polymer layer.

The molecular structure of MATS is shown in Figure 1a. The merits of MATS include its good solubility in common organic solvents, such as toluene, hexane, and acetonitrile, and its relatively high decomposition temperature (approximately 220 °C). Because MATS has a melting temperature of approximately 56 °C, frozen-junction devices can be prepared for operation at room temperature.

For device fabrication, the materials were used as received without further purification. MATS and superyellow were both dissolved into toluene at a weight ratio of 1:50 in a nitrogen-filled glove-box (oxygen level under 3 ppm); the total concentration of the solution was 6 mg mL^{−1}. Solid thin films were prepared by spin-casting from this solution in the glove-box. Superyellow and superyellow with 2 wt % MATS show strong photoluminescence (PL) both in solution and in the solid state with almost identical spectra. Figure 2 shows the

[*] Dr. Y. Shao, Prof. A. J. Heeger, Prof. G. C. Bazan
Institute for Polymers and Organic Solids
and Mitsubishi Center for Advanced Materials
University of California, Santa Barbara
Santa Barbara, CA 93106 (USA)
E-mail: sy@physics.ucsb.edu; ajhe@physics.ucsb.edu

[**] This research was supported by a UC Discovery grant as part of the Mitsubishi Chemicals Center for Advanced Materials (MC-CAM) at UC Santa Barbara. We thank Dr. Daniel Moses and Nelson Coates for help in obtaining the response time of the frozen junction devices. We also thank James Swensen and Jonathan D. Yuen for technical help and discussion.

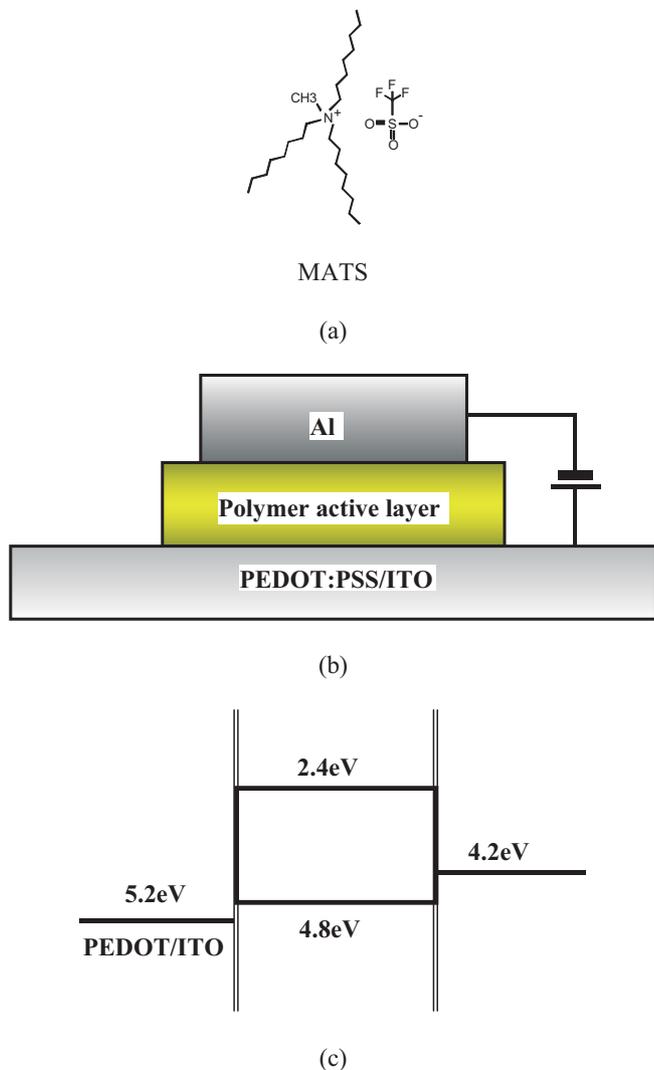


Figure 1. a) The molecular structure of MATS. b) The device architecture. c) The schematic energy-level diagram for the open-circuit status.

PL spectra of superyellow containing 2 wt % MATS (solid lines) and pure superyellow (dashed lines) both in solution (Fig. 2a) and as solid thin films (Fig. 2b).

Polymer light-emitting devices were fabricated on patterned ITO-coated glass substrates, which had been cleaned by successive ultrasonic treatment in detergent, acetone, and isopropyl alcohol. The ITO glass was then subjected to UV-ozone treatment for about 30 min. A thin layer of PEDOT-PSS film was spin-cast onto the ITO glass substrate with a spin speed of 4000 rpm for 1 min and then baked at 120 °C for 20 min in ambient conditions. The polymer layers were then spin-cast from the solution containing a 1:50 weight ratio of MATS and superyellow in toluene (spin speed of 1500 rpm) for 1 min in the nitrogen glove-box. The Al cathode was evaporated through a shadow mask with an active area of approximately 14.8 mm² (vapor deposition of the aluminum cathode was carried out under a base pressure of ca. 1 × 10⁻⁶ torr with deposition rates of about 4 Å s⁻¹;

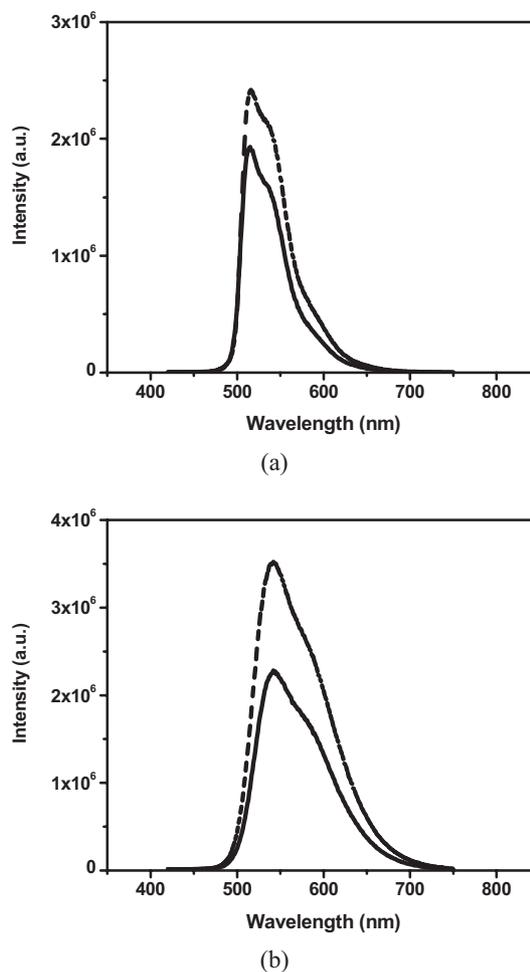


Figure 2. The photoluminescence spectra of 2 wt % MATS in superyellow (solid lines) and pure superyellow (dashed lines) in a) 6 mg mL⁻¹ toluene solution and b) solid thin films.

1 torr = 133.322 Pa). Schematic diagrams of the device structure and the relevant energy levels of the various components (for open circuit conditions) are shown in Figure 1b and c.

All electrical measurements were performed under nitrogen in the glove-box. The current-voltage (*I-V*) characteristics were recorded by using a computer-controlled Keithley 236 source-measure unit (SMU). When the devices were tested for the first time without any prior heat treatment, their behavior was just like that of a PLED with Al as a cathode: the turn-on voltage was over 6 V with relatively low brightness and low efficiency even at a high operating voltage. Under 4 V forward bias, the current was in the range of a few microamps per centimeter squared. The electrical behavior was asymmetric (characteristic of a diode). Light emission was not observed in reverse bias.

When the devices were heated to around 80 °C under 4 V forward bias, the current increased by approximately three orders of magnitude and reached 10 mA cm⁻² in one minute. The current-rectification factor also improved by about two orders of magnitude and reached about 10⁴ (see Fig. 3). The

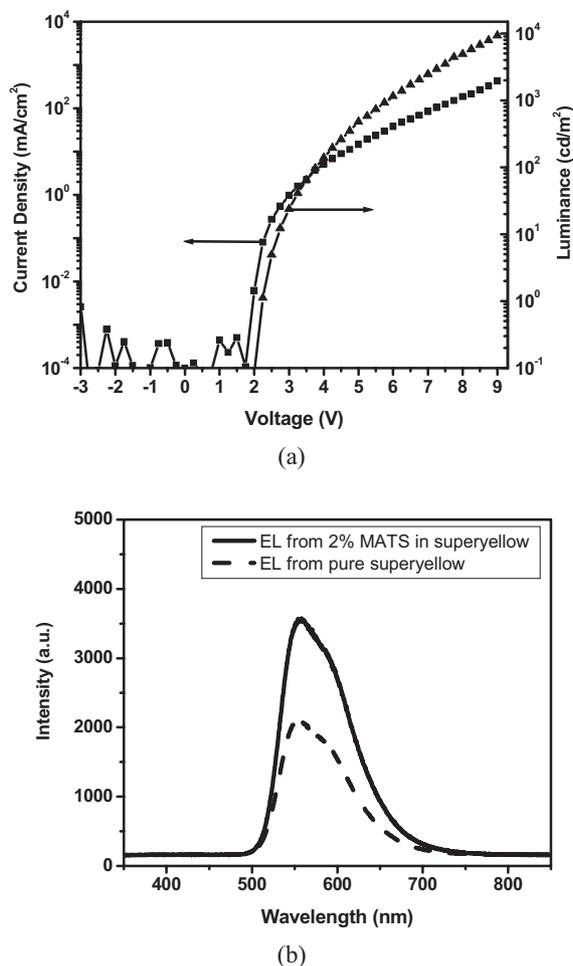


Figure 3. a) I - V and brightness-voltage (B - V) curves of the device ITO/PEDOT/2 wt % MATS in superyellow/Al. b) The EL spectrum of the ITO/PEDOT/2 wt % MATS in superyellow/Al devices is shown as the solid line, and the EL spectrum of the reference device (ITO/PEDOT/superyellow/Al) is shown as the dashed line.

heating temperature was purposely chosen to be above the melting point of MATS and close to the glass-transition temperature (T_g) of superyellow so that ions were generated and could move under the influence of the applied electrical field. The devices were subsequently cooled to room temperature under 4 V forward bias. After cooling, a frozen p-i-n junction was formed in the device. The devices demonstrated excellent performance: high brightness, high efficiency, long continuous operating time, and short response time. More importantly, as LECs, they demonstrated very low turn-on voltage even with the use of a stable cathode material.

Figure 3a shows the current-voltage (I - V) and brightness-voltage (B - V) curves. The turn-on voltages were as low as 2.2 V (turn-on is defined as the voltage required for achieving a brightness of 1 Cd m^{-2}); that is, approximately equal to (or even a little lower than) the bandgap of the superyellow semiconducting polymer.^[16] The junction remained more than 10 h without the application of an electrical field. Leakage currents below turn-on were quite small ($10^{-7} \text{ A cm}^{-2}$). The

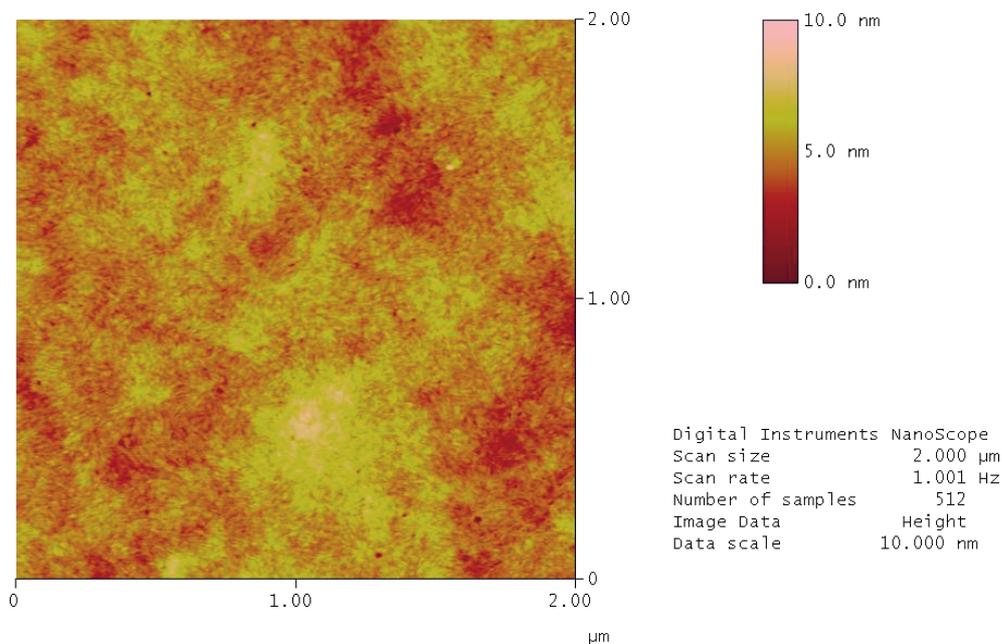
brightness reached $10\,000 \text{ Cd m}^{-2}$ at around 9 V. As shown in Figure 3b, the light emission was from superyellow with almost identical EL spectrum as that obtained from the reference superyellow PLED with the following device structure: ITO/PEDOT/superyellow/Al. The device efficiency was approximately 3.3 Cd A^{-1} (at 5 V with about 500 Cd m^{-2} brightness), which is similar to the efficiency of our control PLED (maximum efficiency is about 4.5 Cd A^{-1}) with the same superyellow as emitting polymer and Ba as cathode.

The use of chemical additives is known to play an important role in electron injection, carrier transport, and exciton energy confinement.^[4,17-19] When two or more materials are used in a blend, the material compatibility or mutual solubility is one of the keys to high-performance devices, especially for long-time operation.^[20,21] Therefore, the proper selection of organic material components is an important issue.

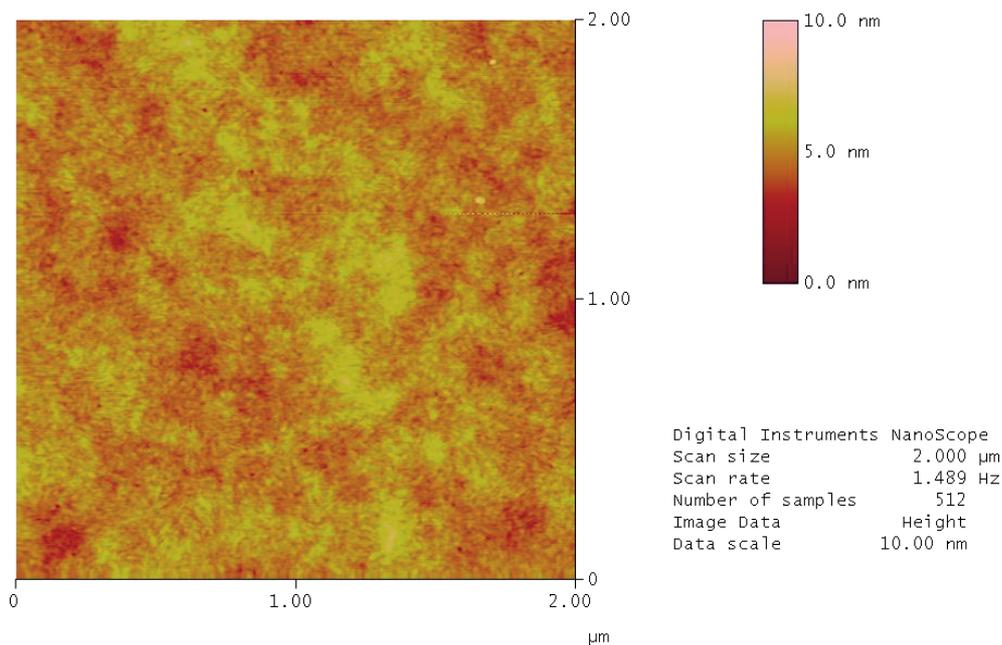
We found that MATS shows excellent compatibility with superyellow. This was confirmed by using atomic force microscopy (AFM) studies, as shown in Figure 4a. Figure 4b shows the AFM image of the control film of pure superyellow. Both were prepared on top of PEDOT-PSS coated ITO glass with a spin speed of about 1500 rpm and then baked on a hot plate at 80°C for about 25 min in the glove-box. Then both films were stored in the glove-box for about 12 days before measurement so that any possible phase separation could develop. Phase separation should be easily identifiable; in the AFM images, there is no evidence of phase separation. The two films showed high surface quality and similar morphologies with similar uniformity, grain size, and height variation. The room-mean-square (RMS) roughness of both is about 0.7 nm, which means they remained quite smooth after a relatively long storage time.

The single-phase nature implied that the system was thermodynamically stable, one of the key characteristics of stable material systems. Phase separation exists in almost all the materials used previously in PLECs, including nanostructure multiphase complexes,^[22] interpenetrating networks,^[14] needle-shaped fronts,^[12] spherical aggregates,^[11] and large-scale topographical separation.^[23] In our emitting layer, the MATS comprised only 2 wt % in the solid thin films. As a result of the good solubility of MATS in superyellow, the films exhibited properties almost identical to those of pure superyellow films. The single-phase stability of this material system with the ionic-liquid additive is the most important reason for the long operating lifetime of the devices.

In order to investigate the origin of the diode junction inside the device during operation, photovoltaic effect measurements were performed and the open-circuit voltages (V_{OC}), which provide information on the built-in potentials of the device, were recorded. Figure 5 shows the I - V curves of the photovoltaic effects before and after device operation. The original V_{OC} of the devices was around 1.25 V and there was almost no V_{OC} change after thermal treatment at 80°C for about 1 min. The I - V curves of the devices before and after heating were nearly identical. The formation of the junction is obvious in the data; when devices were heated to



(a)



(b)

Figure 4. AFM images for the thin films of a) 2 wt% MATS in superyellow and b) pure superyellow.

around 80 °C under 4 V forward bias and cooled to room temperature, the V_{OC} increased by about 0.55 V to 1.8 V. The measured V_{OC} of about 1.8 V is comparable to the bandgap of the emitting polymer. As a result of the electrochemical doping near the anode and cathode interfaces, there were very small barriers for both electron and hole injection and consequently device turn-on voltages were very close to the band-

gap of the semiconducting polymer.^[2,3,24] This advantage reflects one of the most important characteristics of PLECs.

LECs fabricated with the MATS ionic liquid as the source of mobile ions exhibited long continuous operating lifetimes. Data showing the brightness versus time (at room temperature) are shown in Figure 6a (with a constant current density of 6.76 mA cm⁻²). The slow turn-on is indicative of the time

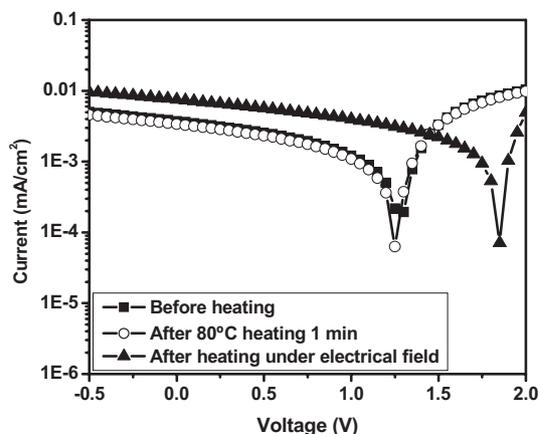


Figure 5. *I*-*V* curves showing the photovoltaic effects of the devices before heating (■), after 80 °C heating for 1 min (○), and after 80 °C heating under 4 V forward bias (▲).

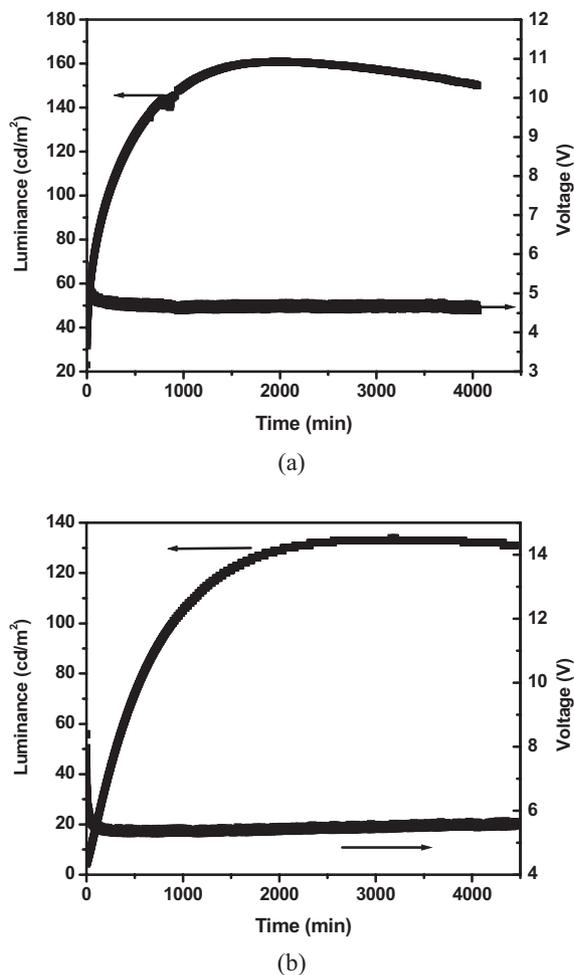


Figure 6. a) Brightness versus time for the device ITO/PEDOT/2 wt% MATS in superyellow/Al (continuous-operation mode). b) Brightness versus time for the device ITO/PEDOT/1.6 wt% MATS + 20 wt% PS in superyellow/Al (continuous-operation mode).

required to form the p-i-n junction at room temperature (i.e., without preheating under bias). Independent measurements of the decay of the preformed p-i-n junction occurred at room temperature over the same time scale. Note, however, that the turn-on time (and junction formation time) was only approximately 1 min at 80 °C. After forming the p-i-n junction by preheating under bias, devices were operated continuously in the glove-box (without packaging) for several days without significant degradation in brightness. Longer-term lifetime measurements are underway.

The operating lifetime can be further enhanced by introducing more stable components, for example, high T_g polymers, into this system. The frozen junction after redox and ion redistribution can also be further stabilized by the addition of high T_g components. High-molecular-weight polystyrene (PS), molecular weight $M_w = 1 \times 10^6$, has a T_g of about 110 °C. High-molecular-weight PS can be utilized to enhance the stability of LECS fabricated from MATS without introducing phase separation because of the excellent compatibility of PS and superyellow. High-molecular-weight PS was dissolved into toluene and then blended with the previously described superyellow solution containing 2 wt% MATS. The weight ratio of PS and superyellow was 1:4 and consequently the weight percent of MATS in the solution was diluted to 1.6 wt%. Thin-film formation and device fabrication processes were exactly the same as described above. The brightness versus time for a superyellow/PS (1:4) device is shown in Figure 6b. After 200 h, the decay relative to the peak is less than 15 wt%. After sealing with epoxy and a glass cover slide, LECs with MATS (and with PS) were operated continuously in air for several weeks. Again, longer-term lifetime measurements are underway.

Device response time is another important characteristic of frozen-junction PLEC devices. To check the response time, devices were driven with a 6.3 V pulse train at 152 Hz with 43% duty cycle at room temperature, and the light output was measured with a photodetector (peak brightness ca. 1000 Cd m⁻²). The response time was less than 2 ms and consistent with the resistance capacitance (RC) time constant of the device (data not shown).

In summary, polymer light-emitting devices with an ionic liquid blended into the semiconducting polymer have been demonstrated. After the frozen junction was formed, the devices exhibited all the good characteristics of both PLEDs and PLECs including excellent current rectification (ca. 10^4), fast response (<2 ms), high brightness (>10 000 Cd m⁻²), high efficiency (ca. 3.3 Cd A⁻¹), low turn-on voltage (2.2 V), stable cathodes, and long operating lifetimes.

Experimental

Device Fabrication: Polymer light-emitting devices were fabricated on patterned ITO-coated glass substrates, which had been cleaned by successive ultrasonic treatment in detergent, acetone, and isopropyl alcohol. The ITO glass was then subjected to UV-ozone treatment

for about 30 min. A thin layer of PEDOT-PSS film (ca. 40 nm) was spin-cast onto the ITO glass substrate with a spin speed of 4000 rpm for 1 min and then baked at 120 °C for 20 min in ambient conditions. The polymer layers were then spin-cast from the solution containing a 1:50 weight ratio of MATS and superyellow in toluene (with a spin speed of 1500 rpm) for 1 min in the nitrogen glove-box. The thickness of the superyellow layer was about 50 nm. The Al cathode was evaporated through a shadow mask with an active area of approximately 14.8 mm² (vapor deposition of the aluminum cathode was carried out under a base pressure of ca. 1 × 10⁻⁶ torr with deposition rates about 4 Å s⁻¹).

Device Characterization: All electrical measurements were performed under nitrogen in the glove-box. The *I-V* characteristics were recorded by using a computer-controlled Keithley 236 SMU. The photocurrent was measured under an air mass (AM) of 1.5 solar illumination at 100 mW cm⁻² (1 sun) in a nitrogen glove-box. The response time of the device was measured using a HP8011A pulse generator, a 1 mm² silicon photodetector, and a Tektronix 768 Oscilloscope.

Received: September 13, 2006

Revised: October 16, 2006

Published online: January 9, 2007

- [1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* **1990**, 347, 539.
- [2] Q. B. Pei, G. Yu, C. Zhang, Y. Yang, A. J. Heeger, *Science* **1995**, 269, 1086.
- [3] Q. B. Pei, Y. Yang, G. Yu, C. Zhang, A. J. Heeger, *J. Am. Chem. Soc.* **1996**, 118, 3922.
- [4] X. Gong, S. Wang, D. Moses, G. C. Bazan, A. J. Heeger, *Adv. Mater.* **2005**, 17, 2053.
- [5] J. Liu, Q. G. Zhou, Y. X. Cheng, Y. H. Geng, L. X. Wang, D. G. Ma, X. B. Jing, F. S. Wang, *Adv. Funct. Mater.* **2006**, 16, 957.
- [6] G. Yu, Y. Cao, M. Andersson, J. Gao, A. J. Heeger, *Adv. Mater.* **1998**, 10, 385.
- [7] J. Gao, Y. F. Li, G. Yu, A. J. Heeger, *J. Appl. Phys.* **1999**, 86, 4594.
- [8] J.-H. Shin, S. Xiao, Å. Fransson, L. Edman, *Appl. Phys. Lett.* **2005**, 87, 043 506.
- [9] Y. Kervella, M. Armand, O. Stephan, *J. Electrochem. Soc.* **2001**, 148, H155.
- [10] Y. Cao, Q. B. Pei, M. R. Andersson, G. Yu, A. J. Heeger, *J. Electrochem. Soc.* **1997**, 144, L317.
- [11] C. H. Yang, Q. J. Sun, J. Qiao, Y. F. Li, *J. Phys. Chem. B* **2003**, 107, 12 981.
- [12] J.-H. Shin, S. Xiao, L. Edman, *Adv. Funct. Mater.* **2006**, 16, 949.
- [13] L. Edman, B. Liu, M. Vehse, J. Swensen, G. C. Bazan, A. J. Heeger, *J. Appl. Phys.* **2005**, 98, 044 502.
- [14] Y. Cao, G. Yu, A. J. Heeger, C. Y. Yang, *Appl. Phys. Lett.* **1996**, 68, 3218.
- [15] H. Spreitzer, H. Becker, E. Kluge, W. Kreuter, H. Schenk, R. Schmidt, H. Schoo, *Adv. Mater.* **1998**, 10, 1340.
- [16] J. C. de Mello, N. Tessler, S. C. Graham, R. H. Friend, *Phys. Rev. B: Condens. Matter* **1998**, 57, 12 951.
- [17] Y. Hamada, H. Kanno, T. Tsujioka, H. Takahashi, T. Usuki, *Appl. Phys. Lett.* **1999**, 75, 1682.
- [18] Y. Shao, Y. Yang, *Appl. Phys. Lett.* **2005**, 86, 073 510.
- [19] T.-H. Kim, H. K. Lee, O. O. Park, B. D. Chin, S.-H. Lee, J. K. Kim, *Adv. Funct. Mater.* **2006**, 16, 611.
- [20] L. D. Bozano, K. R. Carter, V. Y. Lee, R. D. Miller, R. DiPietro, J. C. Scott, *J. Appl. Phys.* **2003**, 94, 3061.
- [21] Y. Shao, Y. Yang, *Adv. Funct. Mater.* **2005**, 15, 1781.
- [22] L. Edman, M. Pauchard, D. Moses, A. J. Heeger, *J. Appl. Phys.* **2004**, 15, 4357.
- [23] Y. F. Hu, C. Tracy, J. Gao, *Appl. Phys. Lett.* **2006**, 88, 123 507.
- [24] L. Edman, M. A. Summers, S. K. Buratto, A. J. Heeger, *Phys. Rev. B: Condens. Matter* **2004**, 70, 115 212.