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Ionic Liquid Used in Long-Lifetime Polymer Light-Emitting Electrochemical Cells

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1. Introduction

Polymer light-emitting devices have been divided into two general types: polymer light-emitting diodes (PLEDs) and polymer light-emitting electrochemical cells (PLECs). (Burroughes et al., 1990; Pei et al., 1995; Pei et al., 1996; Gong et al., 2005; Liu et al., 2006;) The advantages for PLEDs include 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 band gap 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 (time required for the mobile ions to diffuse during junction formation). A solution to this problem is to “freeze” the junction after ion redistribution. (Yu et al., 1998; Gao et al., 1999;) 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. (Shin et al., 2005; Kervella et al., 2001)

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 band gap 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. (Pei et al., 1995; Pei et al., 1996) Crown ethers (and derivatives) (Kervella et al., 2001; Cao et al., 1997) and other organic salts (Yang et al., 2003; Shin et al., 2006) 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. (Edman et al., 2005) For almost all PLECs, the additives comprise at least 5 weight percent. More important, 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-i-n junction of the LEC, ions must move from one phase into the other; e.g. from the PEO into the luminescent polymer. This phase separation appears to degrade the device performance, especially the lifetime. (Cao et al., 1997) The phase separation results from the relatively poor compatibility of the ionic materials (hydrophilic) with 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. (Cao et al., 1996) 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. (Edman et al., 2005)

2. Long-lifetime polymer light-emitting electrochemical cells with ionic liquid

2.1 Material selection

In the devices described here, we utilized the simplest sandwich structure for the device configuration with poly(3,4-ethylenedioxythiophene)-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) (Spreitzer et al., 1998) was selected as our host light-emitting polymer and an organic ionic liquid, methyltrioctylammonium 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 Fig.1 (a). 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.

2.2 Device fabrication

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 3ppm); the total concentration of the solution was 6mg/mL. Solid thin films were prepared by spin casting from this solution in the glove box. Superyellow and superyellow with 2wt% MATS show strong photoluminescence (PL) both in solution and in the solid state with almost identical spectra. Fig. 2 shows the PL spectra of superyellow containing 2wt% MATS (solid lines) and pure superyellow (dash lines) both in solution (Fig. 2(a)) and as solid thin films (Fig. 2 (b)).

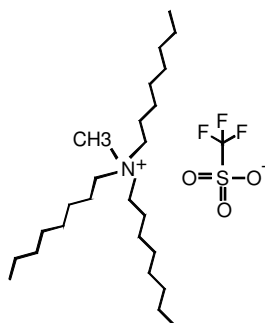


Fig. 1. (a)

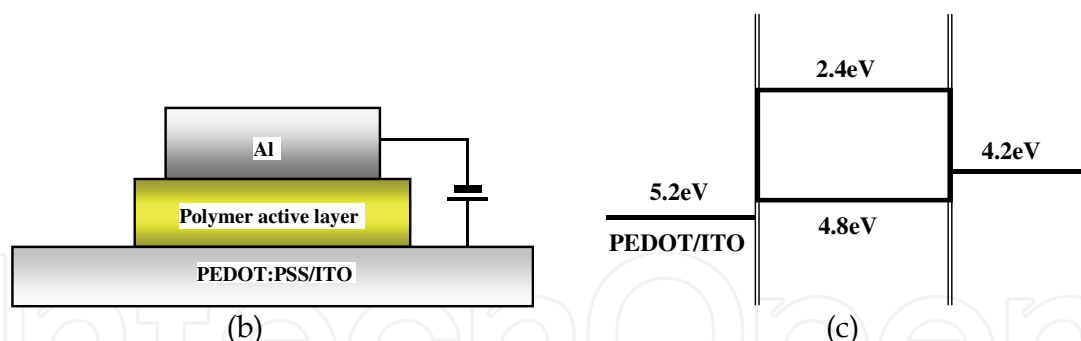


Fig. 1. (a) Molecular structures of methyltrioctylammonium trifluoromethanesulfonate (MATS). (b) Device architecture. (c) Schematic energy level diagram for the open circuit status.

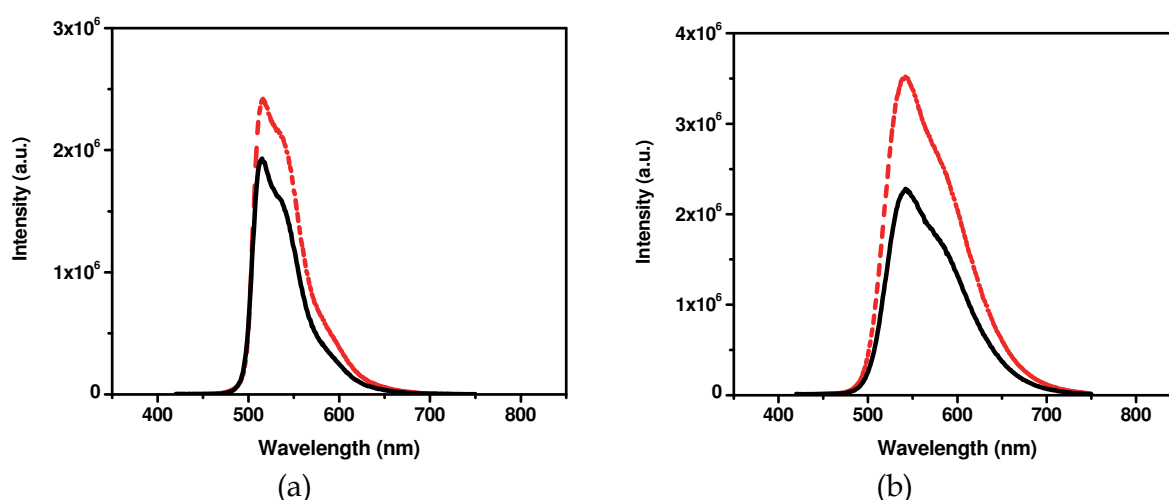


Fig. 2. Photoluminescence spectra of 2wt% MATS in superyellow (solid lines) and pure superyellow (dash lines) in (a) 6mg/mL toluene solution and (b) solid thin films.

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 minutes. A thin layer of PEDOT-PSS film was spin-cast onto the ITO glass substrate with a spin speed of 4000 rpm for 1 minute and then baked at 120 °C for 20 minutes in ambient. The polymer layers were then spin-cast from the solution containing 1:50 weight ratio of MATS and superyellow in toluene (spin-speed of 1500 rpm) for 1 minute 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 $\sim 1 \times 10^{-6}$ Torr with deposition rates about 4 Å/s). Schematic diagrams of the device structure and the relevant energy levels of the various components (for open circuit conditions) are shown in Fig. 1(b) and (c).

2.3 Device measurement

All electrical measurements were performed under nitrogen in the glove box. The current-voltage (I-V) characteristics were recorded by 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 cathode: the turn-on voltage was over 6 volts with relatively low brightness and low efficiency even at high

operating voltage. Under 4V forward bias, the current was in the range of a few $\mu\text{A}/\text{cm}^2$. 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 4V forward bias, the current increased by approximately three orders of magnitude and reached $10\text{mA}/\text{cm}^2$ in one minute. The current-rectification factor also improved by about two orders of magnitude and reached to about 10^4 (see Fig 3). The 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 important, as LECs, they demonstrated very low turn-on voltage even with the use of a stable cathode material.

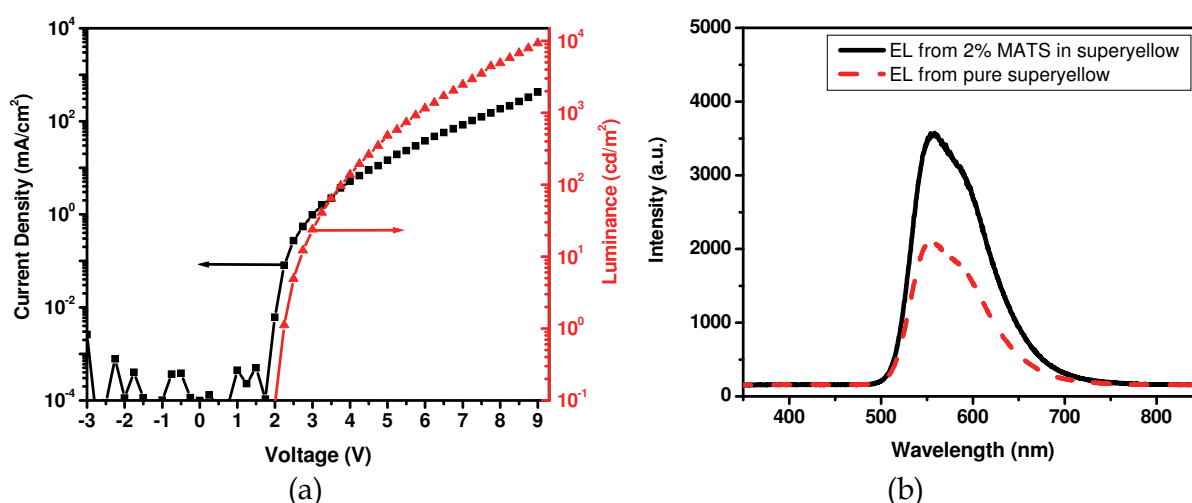


Fig. 3. (a) Current-voltage (I-V) and brightness-voltage (B-V) curves of device ITO/PEDOT/2wt% MATS in superyellow/Al. (b) The EL spectrum of the ITO/PEDOT/2% MATS in superyellow/Al devices is shown as the solid line, and the EL spectrum of the reference device (ITO/PEDOT/superyellow/Al) is shown as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

Fig. 3(a) shows the I-V and brightness-voltage (B-V) curves. The turn-on voltages are as low as 2.2V (turn-on defined as the voltage required for achieving a brightness of $1\text{cd}/\text{m}^2$); i.e. approximately equal to (or even a little lower than) the band gap of the superyellow semiconducting polymer. (deMello et al., 1998) The junction remained for more than 10 hours without application of an electrical field. Leakage currents below turn-on are quite small ($10^{-7}\text{A}/\text{cm}^2$). The brightness reached $10,000\text{cd}/\text{m}^2$ at around 9V. As shown in Fig. 3(b), the light emission is 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 $3.3\text{cd}/\text{A}$ (at 5V with about $500\text{cd}/\text{m}^2$ brightness), which is similar to the efficiency of our control PLED (maximum efficiency is about $4.5\text{cd}/\text{A}$) with the same superyellow as emitting polymer and Ba as cathode.

2.4 Phase separation research in active layer

The use of chemical additives is known to play an important role in electron injection, carrier transport, and exciton energy confinement. (Gong et al., 2005; Hamada et al., 1999;

Shao and Yang, 2005; Kim et al., 2006) 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. (Bozano et al., 2003; Shao and Yang, 2005) Therefore, the proper selection of organic material components is an important issue.

We find that MATS shows excellent compatibility with superyellow. This was confirmed by atomic force microscope (AFM) studies as shown in Fig. 4(a). Fig. 4 (b) 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 1500rpm and then baked on hot plate at 80°C for about 25 minutes 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 can develop. Phase separation should be easily identified. In the AFM pictures, there is no evidence of phase separation. The two films show high surface quality and similar morphologies with similar uniformity, grain size, and height variation. The room-mean-square (RMS) roughness of both is about 0.7nm, which means they remain quite smooth after relatively long time storage. (Wenzl et al., 2004)

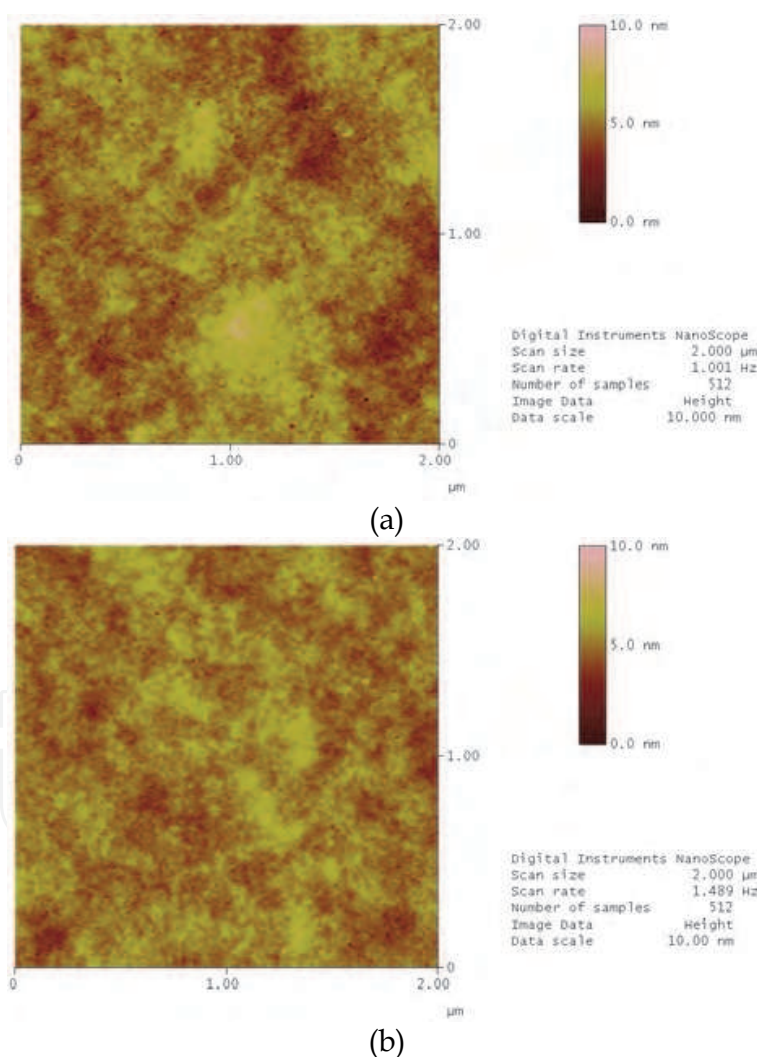


Fig. 4. Atomic force microscope (AFM) images for the thin films of (a) 2wt% MATS in superyellow and (b) pure superyellow.

The single-phase nature implies that the system is 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 multi-phase complexes, (Edman et al., 2004) interpenetrating networks, (Cao et al., 1996) needle-shaped fronts, (Shin et al., 2006) spherical aggregates, (Yang et al., 2003) and large-scale topographical separation. (Hu et al., 2006) In our emitting layer, the MATS comprises only 2 weight percent 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.

2.5 Origin of open circuit voltage

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. Fig. 5 shows the I-V curves of the photovoltaic effects before and after device operation. The original V_{OC} of the devices is around 1.25V and there is almost no V_{OC} change after thermal treatment at 80 °C for about 1 minute. The I-V curves of the devices before and after heating are nearly identical. The formation of the junction is obvious in the data; when devices were heated to around 80 °C under 4V forward bias and cooled to room temperature, the V_{OC} increased by about 0.55V to 1.8 V. The measured V_{OC} of about 1.8V is comparable to the band gap of the emitting polymer. As a result of the electrochemical doping near the anode and cathode interfaces, there are very small barriers for both electron and hole injection and consequently device turn-on voltages are very close to the band gap of the semiconducting polymer. (Pei et al., 1995; Pei et al, 1996; Edman et al., 2004) This advantage reflects one of the most important characteristics of PLECs.

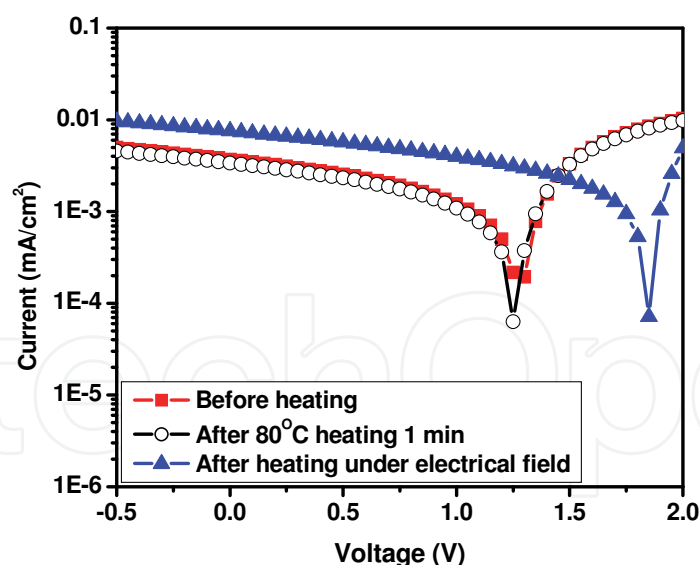


Fig. 5. Current-voltage (I-V) curves showing the photovoltaic effects of the devices before heating (solid square), after 80 °C heating for 1 minute (empty circle), and after 80 °C heating under 4V forward bias (solid triangle).

2.6 Device lifetime and response time

LECs fabricated with the MATS ionic liquid as the source of mobile ions exhibit long continuous operating lifetimes. Data showing the brightness vs time (at room temperature)

are shown in Fig. 6(a) (constant current density at 6.76 mA/cm^2). The slow turn-on is indicative of the time required to form the p-i-n junction at room temperature (i.e. without pre-heating under bias). Independent measurements of the decay of the pre-formed p-i-n junction occurs at room temperature over the same time scale. Note, however, that the turn-on time (and junction formation time) is only approximately one minute at 80°C . After forming the p-type-intrinsic-n-type (p-i-n) junction by pre-heating under bias, devices were operated continuously in the glove box (without packaging) for several days without significant degradation in brightness.

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 (M_w) polystyrene (PS) ($MW \sim 1 \times 10^6$) has a glass transition temperature of about 110°C . High molecular weight PS can be utilized to enhance the stability of LECS made with 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 2wt% MATS. The weight ratio of PS and superyellow was 1:4 and consequently the weight percent of MATS in the solution was diluted to 1.6wt%. Thin film formation and device fabrication processes were exactly same as described above. The brightness vs time for a superyellow:PS (1:4) device is shown in Fig 6(b). After 200 hours, the decay relative to the peak is less than 15wt%. After sealing with epoxy and a glass cover slide, LECS with MATS (and with PS) were operated continuously in air for several weeks.

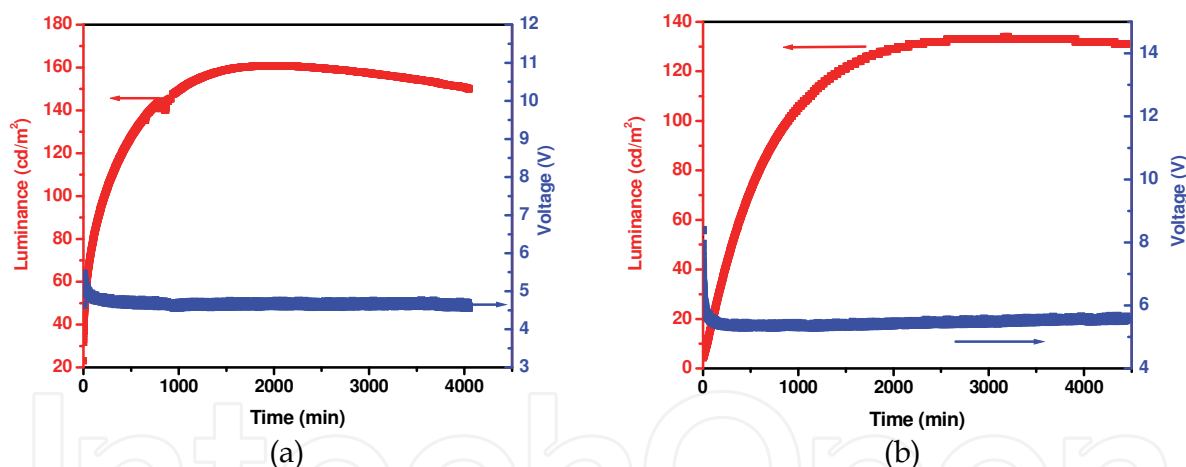


Fig. 6. (a) Brightness vs time for the device ITO/PEDOT/2%MATS in superyellow/Al (continuous operation mode). (b) Brightness vs time for the device ITO/PEDOT/1.6%MATS + 20% PS in superyellow/Al (continuous operation mode).

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

2.7 Summary

In summary, polymer light-emitting devices with an ionic liquid blended into the semiconducting polymer have been demonstrated. After the frozen junction is formed, the

devices exhibit all the good characteristics of both PLEDs and PLECs including excellent current-rectification ($\sim 10^4$), fast response ($< 2\text{ms}$), high brightness ($> 10,000\text{ cd/m}^2$), high efficiency ($\sim 3.3\text{cd/A}$), low turn-on voltage (2.2V), stable cathodes, and long operating lifetimes.

3. LED to LEC transition behavior in polymer light-emitting devices

3.1 Introduction for operation mechanism of polymer LED and LEC

Polymer light-emitting diodes (Braun & Heeger, 1991) and polymer light-emitting electrochemical cells (Pei et al., 1995; Pei et al., 1996) are of interest because of their potential applications in solid state lighting and in high information content displays. The two types of devices (LEDs and LECs) have different operating mechanisms. In PLECs, the anions and cations redistribute inside the active polymer layer under the influence of an applied electric field with associated electrochemical redox doping (n-type near the cathode and p-type near the anode). As a result of the electrochemical doping, a light-emitting junction with a built-in potential is formed. However, the ion redistribution is a relatively slow process compared with electron or hole transport in semiconducting polymers. Therefore, PLECs typically show a continuous (and slow) increase in emission after the electric field is applied. In PLEDs, the use of a low work function metal as the cathode material facilitates electron injection at the semiconductor interface. Thus, in PLEDs, electrons and holes are injected directly from the electrodes into the p^* - and p -bands, respectively; PLEDs are inherently fast-response devices.

3.2 Device fabrication

In this part, polymer light-emitting devices with 2% MATS in superyellow were fabricated with thin films of barium (Ba) as the cathode material. The light-emitting devices were fabricated by spin-casting 6mg/mL superyellow with two weight percent MATS from solution in toluene onto PEDOT-PSS coated ITO glass (spin speed of 1500 rpm). After deposition of the polymer film, 5nm Ba and subsequently 100nm Al were deposited in a vacuum of about 10^{-6} torr . All the device fabrication steps were performed in a nitrogen glove box with oxygen level of about 3ppm . The thickness of the PEDOT-PSS and the active polymer layers were determined by AFM as 40nm and 50nm , respectively. For comparison, PLEDs without MATS were also fabricated under similar identical conditions.

3.2 Device measurement

All electrical measurements were performed under nitrogen in the glove box. The current-voltage characteristics were recorded by a computer controlled Keithley 236 source-measure unit.

Prior to electrochemical doping and p-i-n junction formation, the as-fabricated devices can be considered traditional PLEDs. After several forward scans from 0 to 8 V , the device was “charged” at room temperature by ion redistribution and electrochemical doping. Fig. 7 shows the device I-V curves before and after charging. After charging, the turn-on voltage was 2.18 V ($@1\text{cd/m}^2$), slightly lower than before charging ($2.33\text{V}@1\text{cd/m}^2$). As shown in Fig. 7, before charging the brightness at 4 V was only about 150 cd/m^2 , whereas after charging the brightness at 4 V increased to nearly 600 cd/m^2 . The injected currents also increased by a factor of 4 after charging. The device emission efficiency, therefore, remained at approximately 3 cd/A . As expected, there was no evidence of this kind of charging effect in regular PLEDs with pure superyellow as the active semiconductor polymer.

Fig. 8 shows the transition in operating mechanism from LED to LEC during continuous operation at room temperature. The device was operated in constant current mode at 6.76 mA/cm² without prior charging or heating. The operating voltage was 4.2V at the beginning of the experiment and dropped to below 4V after about 5 minutes; i.e. lower than that of the control PLED with the same constant current (Fig. 9(b)). The brightness initially decreased from 200 cd/m² to 128 cd/m² during approximately 20 minutes. During the same period, the operating voltage dropped from 4.2 V to 3.7 V.

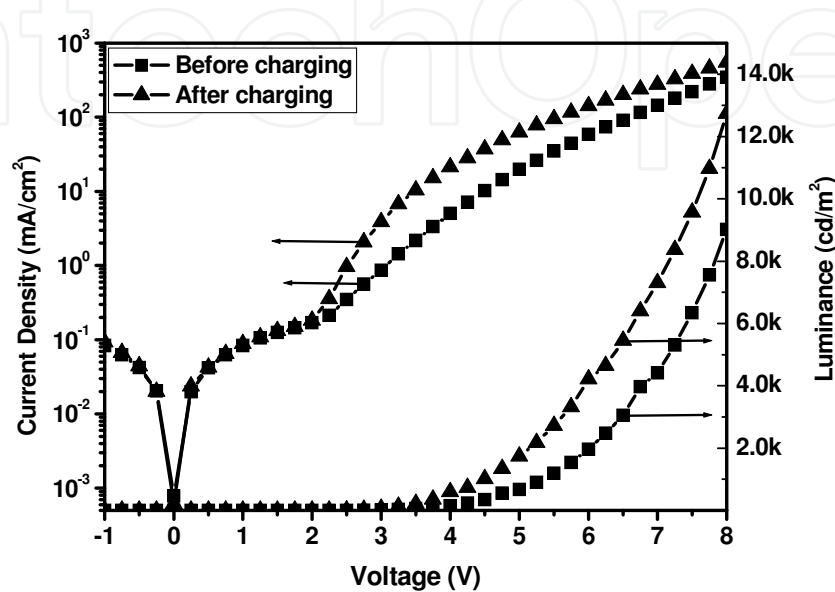


Fig. 7. The current-voltage (I-V) characteristics for the device ITO/PEDOT/2% MATS in superyellow/Ba/Al before and after charging.

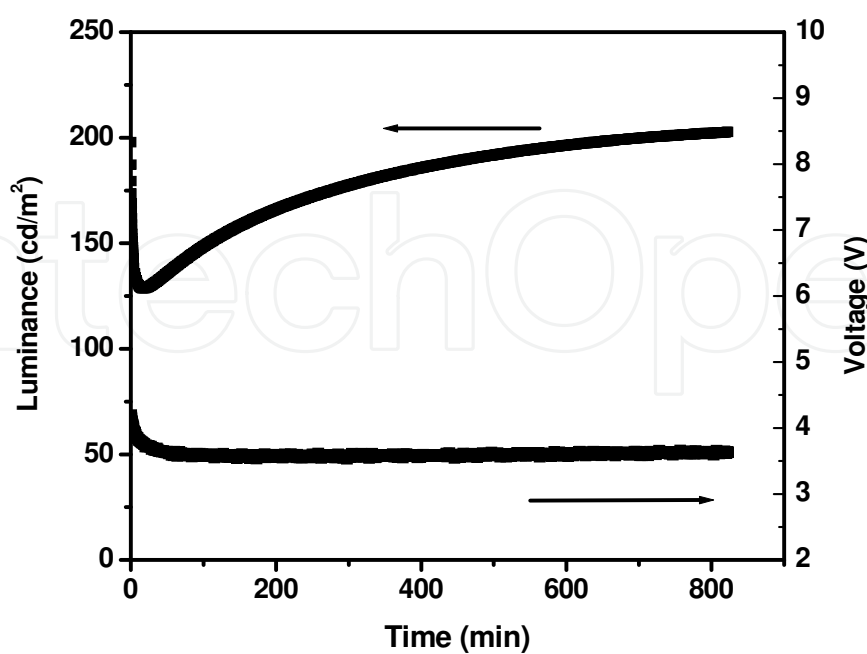


Fig. 8. The current-voltage-brightness (I-V-B) characteristics for the device ITO/PEDOT/2% MATS in superyellow/Ba/Al under continuous operation with constant current.

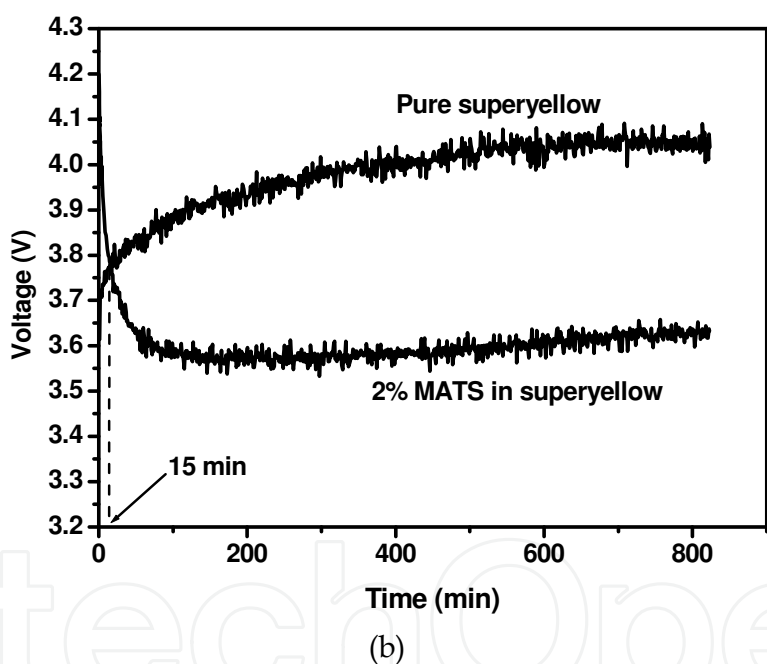
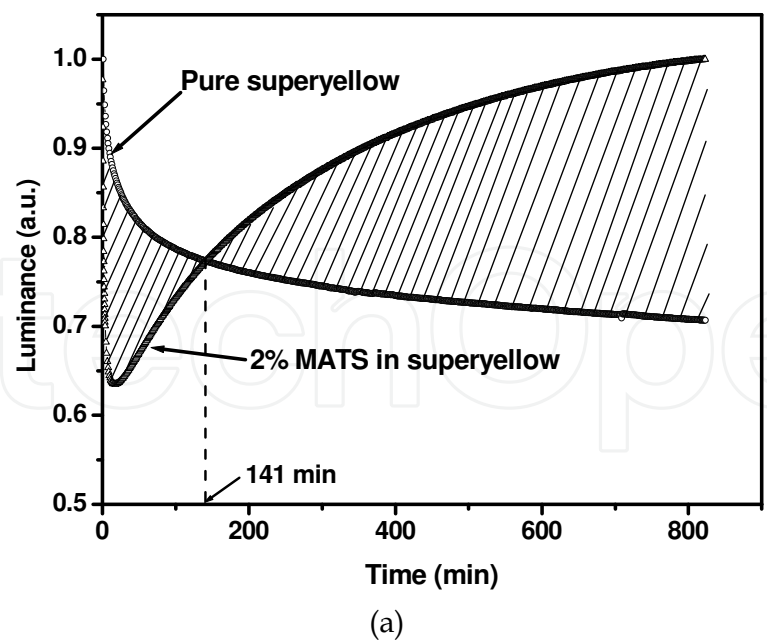


Fig. 9. (a) Comparison for the decay curves of regular PLED with pure superyellow and the device with 2% MATS in superyellow. (b) Comparison for the operational voltage curves of regular PLED with pure superyellow and the device with 2% MATS in superyellow.

3.3 Discussion

The initial rapid turn-on is characteristic of PLED behavior; the degradation of the low work function cathode resulted in a rapid initial decay in brightness. After a short time, however, ion motion and electrochemical redox doping were initiated. As a result of the redox doping, charge injection of both electrons and holes was enhanced. After approximately 20 minutes continuous operation, the degradation of the PLED and the enhancement of the PLEC reached a balance point, and the brightness started to increase.

The initial brightness was fully recovered after 620 minutes continuous operation and continued to slowly increase, reaching the highest point after another two hundred minutes operation. Long term monitoring of the brightness indicated only approximately 10% decay after 10,000 minutes operation (measured with respect to the point of highest brightness); a time of order 1000 times longer than that of the control PLED (for the same 10% decay).

Fig. 9 shows the brightness decay and the increase in operating voltages for the control PLED with pure superyellow and the device with 2% MATS in superyellow. The brightness of device with 2% MATS in superyellow is larger than that of the control PLED after 141 minutes operation, and the corresponding operating voltage is less than that of the control after approximately 15 minutes. In Fig. 9(a), the shadowed area during the initial 141 minutes shows the loss of luminance and the shadowed area after 141 minutes shows the subsequent gain of luminance. As shown the operating voltage for the device with 2% MATS in superyellow is lower than that of the control PLED after 15 minutes continuous operation; see Fig. 9(b). At longer times, the operating voltage for the device with 2% MATS in superyellow remains approximately 0.4V below that of the control PLED.

3.4 Summary

In summary, hybrid polymer light-emitting devices with the combined features of LEDs and LECs were fabricated and investigated. The LED to LEC transition results from the formation of a built-in p-i-n junction. Because of the electrochemical doping (p-type near the anode and n-type near the cathode), both electron and hole injection are improved; the contact resistance and the operating voltage are correspondingly reduced. These hybrid polymer light-emitting devices exhibit fast turn-on with low turn-on voltage, low operating voltage, relatively long lifetime with brightness and efficiency comparable to PLEDs.

4. Long-lifetime polymer light-emitting electrochemical cells fabricated with crosslinked hole transport layers

4.1 Introduction for PLEC decay

The ions play an important role as counterions for the electrochemical doping of the semiconducting polymers in PLECs. This doping generates low-resistance contacts (ohmic contacts in many cases). The high doping levels, however, can lead to degradation of the polymers. (Yang et al., 2003; Hu et al., 2006; Dane and Gao, 2004) As a result, PLECs typically have relatively short device lifetimes, especially at high operating voltages. This lifetime issue remains the biggest obstacle for the applications of PLECs. Currently the doping degradation mechanism is not well understood. The heavy doping and/or related electrochemical side-reactions (Shin et al., 2006; Gao et al., 1997; Edman et al., 2004) in the doped polymer near the electrodes could affect the device stability.

At the interface between polymer layer and anode, hole injection is typically facilitated by casting a thin layer of PEDOT-PSS onto ITO glass. Generally in PLEDs, the injection barrier for holes is relatively lower than that for electrons, as confirmed by studies of “electron-only” and “hole-only” devices. (Parker et al., 1999; Blom et al., 1998) Therefore, in this case, it is not necessary to improve the hole injection by the double-layer/doping. Nevertheless, the redox doping near anode is inevitable since anions and cations are introduced into this system together in the form of neutral ionic materials. It has been suggested that the polymer layer might be degraded by holes from anode. (Blom et al., 1998)

4.2 Crosslinkable hole transport materials

In this part, a thin layer of a crosslinkable hole transport material is introduced into the PLEC structure and inserted between anode and active polymer layer. Therefore, there is no direct contact between anode and doped polymer. We find that the device stability is improved.

The two crosslinkable materials used here are polystyrene(PS) - N,N'-diphenyl-N,N'-bis(4-n-butylphenyl)-(1,1'-biphenyl)-4,4'-diamine(TPD)-perfluorocyclobutane(PFCB) (PS-TPD-PFCB) and 4,4',4''-tris(N-carbazolyl) triphenylamine bis(vinylbenzylether) (VB-TCTA). (Niu et al., 2006; Liu et al., 2000; Zhao et al., 2006; Jiang et al., 2002; Gong et al., 2003) Fig. 10 shows their molecular structures and a schematic diagram of the device structure. The synthesis and characterisation of PS-TPD-PFCB and VB-TCTA were reported elsewhere. (Liu et al., 2000; Zhao et al., 2006; Niu et al., 2007) The advantages of using these two materials include solution-processability and simple thermal crosslinking with no side products involved. Both PS-TPD-PFCB and VB-TCTA were dissolved in 1,2-dichloroethane, and the 0.5 weight percent solutions were spin-cast at 3000rpm to form thin films on the PEDOT:PSS layer. The two-step heating process for crosslinking was conducted in a nitrogen glove box: 100 °C heating for 40 minutes and then 200 °C heating for 1 hour. Thicknesses were determined by atomic force microscopy (AFM); 12 nm for PS-TPD-PFCB layer and 6 nm for VB-TCTA layer. The room-mean-square (RMS) roughness values of the PS-TPD-PFCB and VB-TCTA layers were about 0.5 nm and 1.6 nm, respectively. (Fig. 11(a) and (b))

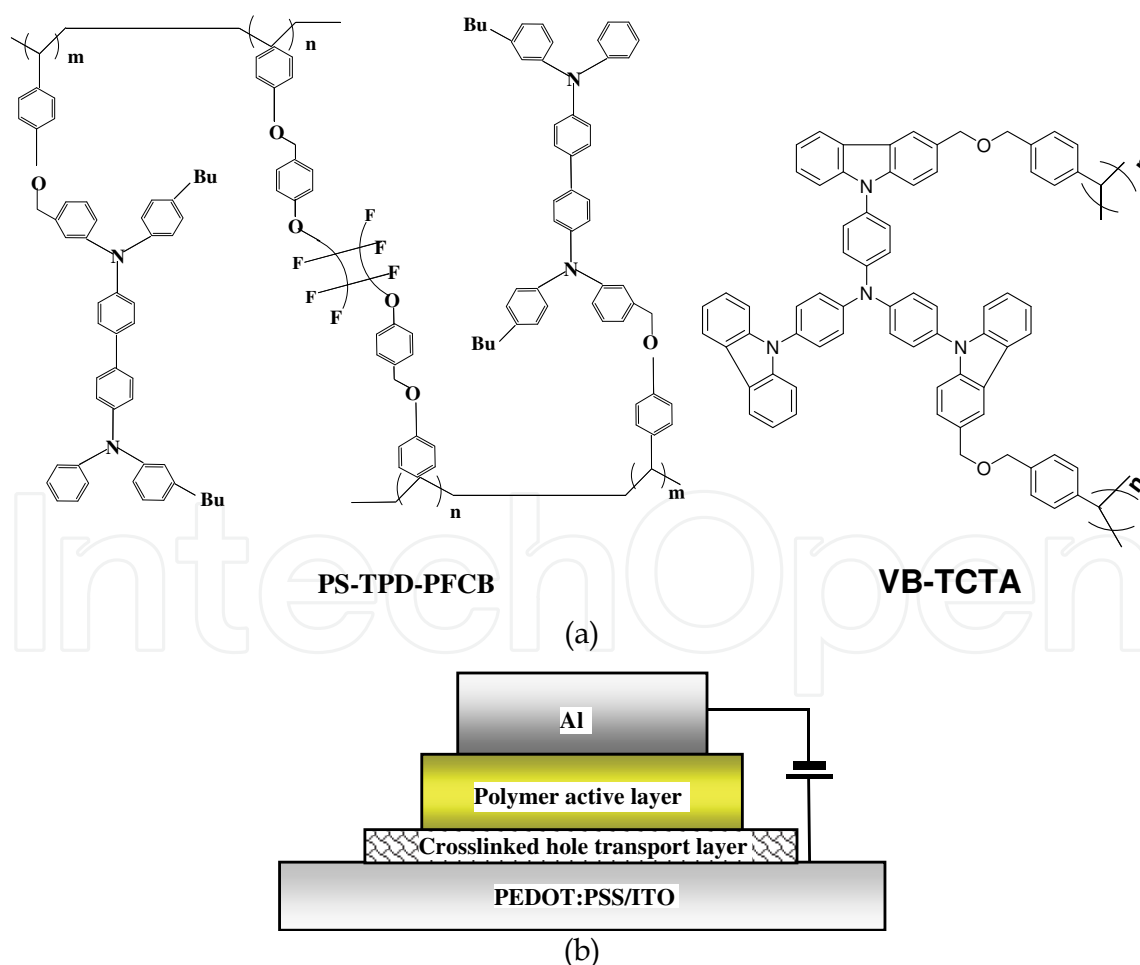


Fig. 10. (a) Molecular structures of PS-TPD and VB-TCTA and (b) Schematic device structure.

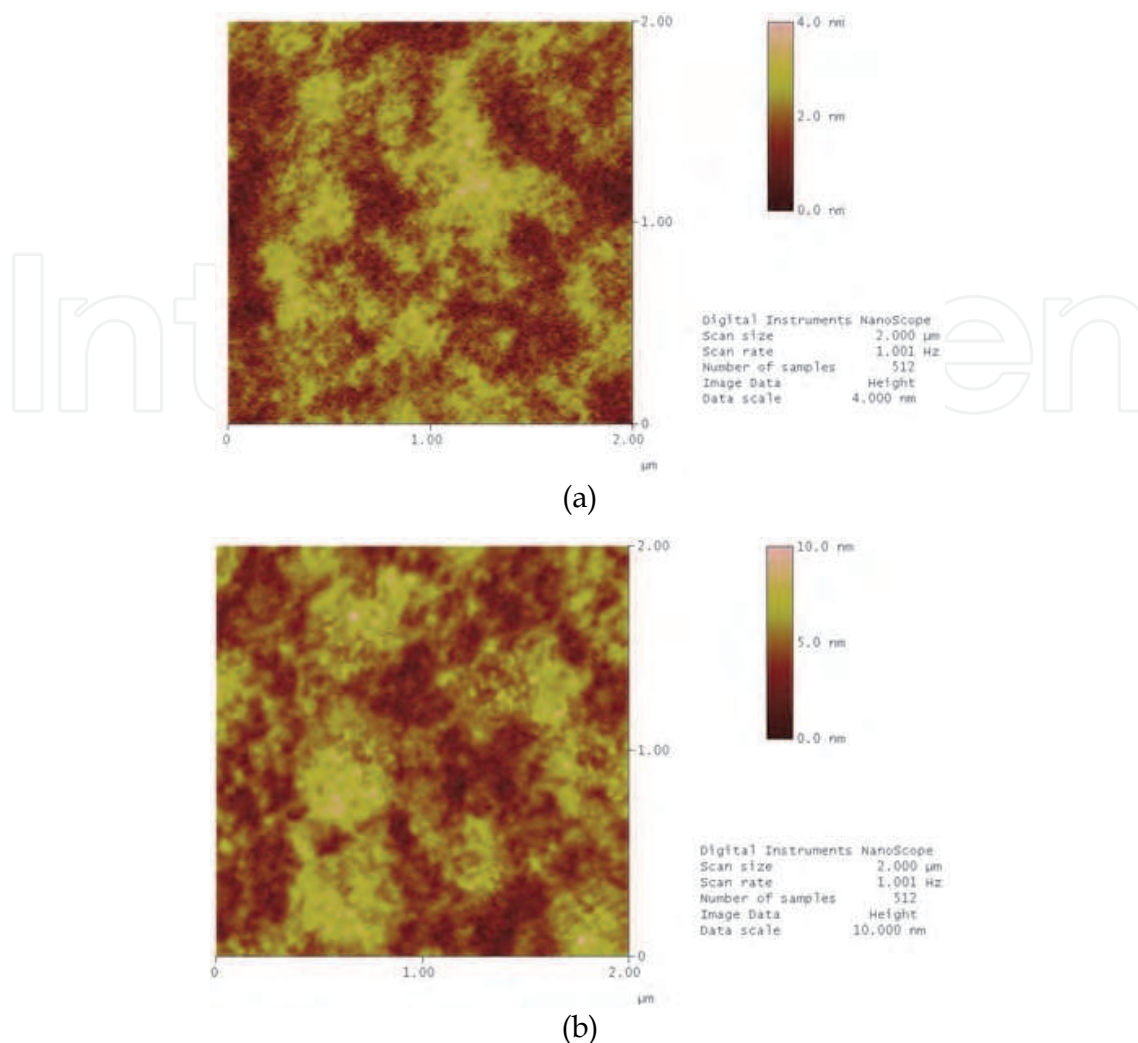


Fig. 11. Atomic force microscope image for (a) PS-TPD and (b) VB-TCTA layers on PEDOT-PSS.

4.3 Device fabrication on crosslinkable hole transport materials

After heating, the crosslinkable hole transport films were cooled to room temperature and 6mg/mL soluble phenyl-substituted superyellow from Merck/Covion with two weight percent MATS as ion source (both in solution in toluene) was spin-cast onto the crosslinked films with a spin speed of 1500 rpm. After annealing the superyellow film at of 80 °C for 30 minutes, 120nm Al was thermally deposited as the cathode under a vacuum of about 10^{-6} torr (1 torr =133Pa) through a shadow mask. The active device area was 14.8 mm². The thickness of the superyellow layer was about 50 nm (determined by AFM). In the following paragraphs, the device with ITO/PEDOT/PS-TPD-PFCB/superyellow:2%MATS/Al is labeled as device A, and the device with ITO/PEDOT/VB-TCTA/superyellow:2%MATS /Al is labeled device B.

4.4 Device measurement

Initially, without pre-bias and heating, the devices showed poor performance; before the ion redistribution, electron injection from Al was poor. After heating at 80 °C under 5V forward bias for about 1.5 minutes, the current increased approximately 1000 times. Then, the devices were cooled to room temperature to freeze in the p-i-n junction. In this process, the

anions moved toward the ITO anode and cations moved toward the Al cathode. In our experiments, the p-i-n junction can survive for about 1 hour at room temperature without significant change in open circuit status after pre-bias. Generally, the device performance is measured within several minutes after the junction is formed and the junction can be considered almost unchanged. As a result, the effects of the double layer or redox doping (depending upon the voltage) improved the electron injection (ionic current only represented a very small part in the total current since ion source was very limited). Note, however, that the anions are blocked from the vicinity of the anode by the crosslinked hole transport layer. The frozen p-i-n junction was stable at room temperature for several hours without external electrical field since MATS has a melting point of 56 °C and superyellow possesses a T_g of around 80 °C.

The existence of the p-i-n junction was confirmed by measuring the built-in potentials of the devices. Photovoltaic effect measurements under AM 1.5 solar illumination at 100 mW/cm² (1 sun) were performed in a nitrogen glove box to obtain V_{OC} as a measure of the built-in potentials. The built-in potentials for the two devices changed significantly after the ion redistribution. Fig. 3 shows the changes of the built-in potentials for the two PLECs. After ion redistribution, the V_{OC} of device A changed from 1.30 V to 1.75 V (Fig. 12(a)) and the V_{OC} of device B changed from 1.15 V to 1.75 V (Fig. 12(b)).

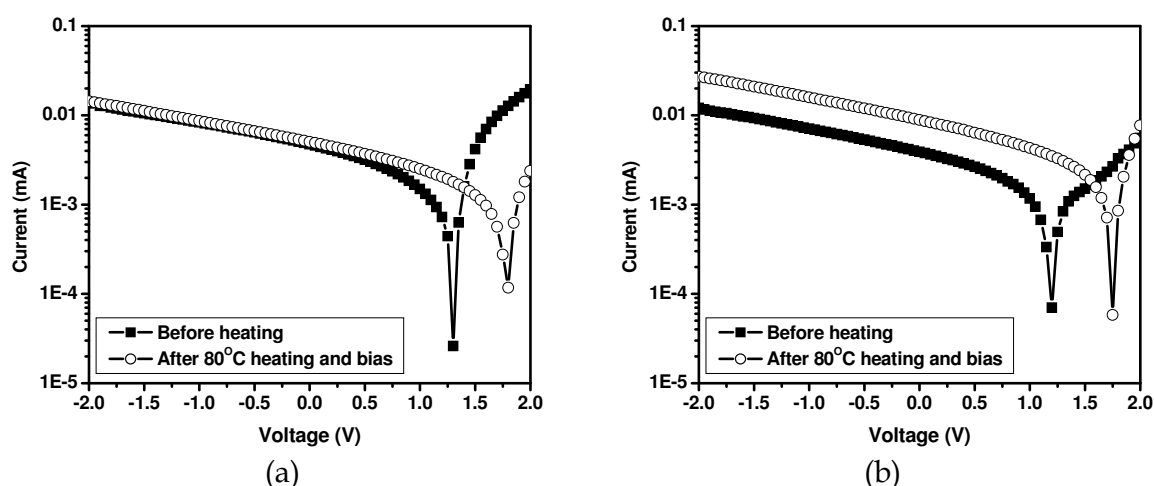
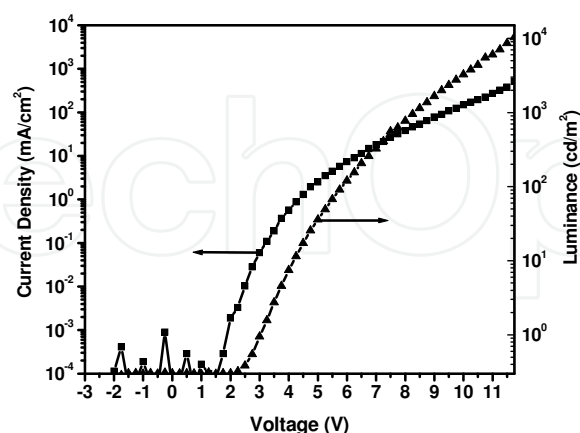


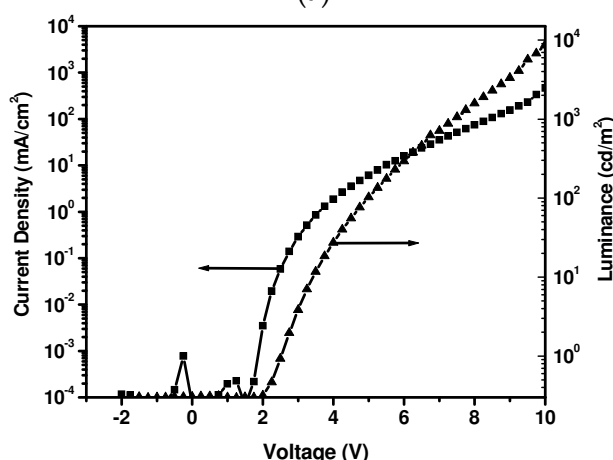
Fig. 12. Current-voltage (I-V) curves showing the photovoltaic effects of the devices before (solid square) and after 80 °C heating under 5V forward bias (circle) for (a) device A and (b) device B.

Fig. 13(a) and (b) show the voltage-current density-brightness curves for device A and device B, respectively. In device A, the turn-on voltage is approximately 3.0V (1 cd/m²) and the maximum brightness is about 10,000 cd/m² at 11.5V. The current efficiency of the device changes from 1.5 cd/A at 4V to 2.5 cd/A at 11V. In device B, the turn-on voltage is approximately 2.5 V (1 cd/m²) and the maximum brightness is about 9000 cd/m² at 9.0 V. The current efficiency again changes from 1.5 cd/A at 4 V to 2.5 cd/A at 9.5 V. In both cases, the current efficiencies increase when the current densities increase, a result which was not seen from traditional PLECs. Control PLECs without the crosslinked hole transport layers were also fabricated and measured. The maximum current efficiency occurred at low operating voltages and the device efficiency decreased slowly as the voltage and current density were increased. We speculate that undesired electrochemical reactions at the anodic interface will be inhibited after insertion of the crosslinked layer. Elimination of electrochemical side-reactions would be

expected to stabilize the p-i-n junction. The crosslinked hole transport layers might also function as electron blocking layers which improve the device efficiency at relatively high voltages when the electron injection is very strong.



(a)



(b)

Fig. 13. Current-voltage (I-V) and brightness-voltage (B-V) curves of (a) device A and (b) device B.

4.5 Device lifetime enhancement and summary

More importantly, the crosslinkable hole transport layers further enhanced the PLEC operating lifetime. All the measurements were performed at room temperature in nitrogen glove box at a constant current density of 6.76 mA/cm^2 . Fig. 14 shows the device decay trends for devices A and B, and the control device without the crosslinked layer. More than 5 devices have been fabricated for each case; Fig. 14 shows the typical results. For device B, after 500 hours the device had not yet reached the point of half brightness. Therefore, we can only conclude that Device B (with the cross-linked hole transport layer) had an even longer lifetime than Device A. All devices were measured from the original status without prior heating. The data clearly illustrate that the lifetimes are enhanced by the crosslinked hole transport layers. Note that Fig. 11 shows that the surfaces of the crosslinked hole transport layers were not very smooth. This surface roughness did not degrade the lifetime; i.e. the lifetime is apparently not very dependent on the surface roughness.

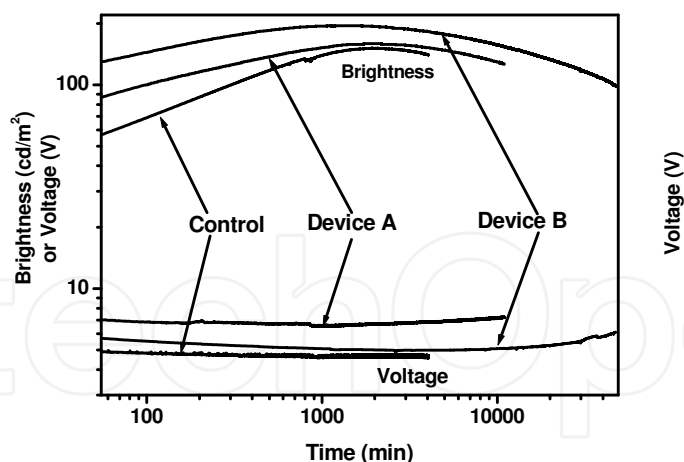


Fig. 14. Brightness vs time (continuous operation mode) for the device A, device B, and control device with structure ITO/PEDOT-PSS/2wt%MATS in superyellow/Al.

In summary, two kinds of crosslinkable hole transport materials have been introduced into the ionic liquid containing PLECs to enhance the performance. By separating the light-emitting layer from conducting PEDOT-PSS layer, the better lifetimes were obtained. The electron injection layer between emitting layer and Al can also be utilized to enhance device lifetime. Titanium sub-oxide sol-gel (TiOx) will be a good choice since it has good stability and hydrophilic property.

5. Conclusion

Ionic liquid has been used in polymer light-emitting electrochemical cells and high performance devices have been successfully demonstrated with long lifetime. With the excellent solubility, good thermal stability, and relatively wide chemical window, ionic liquids can be part of the electrochemical devices. It is believed that more and more ionic liquids and blend systems involving ionic liquids will be discovered.

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Applications of Ionic Liquids in Science and Technology

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This volume, of a two volume set on ionic liquids, focuses on the applications of ionic liquids in a growing range of areas. Throughout the 1990s, it seemed that most of the attention in the area of ionic liquids applications was directed toward their use as solvents for organic and transition-metal-catalyzed reactions. Certainly, this interest continues on to the present date, but the most innovative uses of ionic liquids span a much more diverse field than just synthesis. Some of the main topics of coverage include the application of RTILs in various electronic applications (batteries, capacitors, and light-emitting materials), polymers (synthesis and functionalization), nanomaterials (synthesis and stabilization), and separations. More unusual applications can be noted in the fields of biomass utilization, spectroscopy, optics, lubricants, fuels, and refrigerants. It is hoped that the diversity of this volume will serve as an inspiration for even further advances in the use of RTILs.

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