

Ionic Liquid Doped Polymer Light-Emitting Electrochemical Cells

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The polymer light-emitting electrochemical cells (LECs) were fabricated with MEH–PPV as the luminescent polymer and the ionic liquid of imidazolium salts as the supporting electrolyte. The imidazolium salts utilized include various 1-methyl-3-alkylimidazolium salts with the alkyl substituents of butyl (bmim), dodecyl (dmim), tetradecyl (tmim), or hexadecyl (hmim) and the anions of PF_6^- or BF_4^- , which possess different melting points from room temperature for $[\text{bmim}^+][\text{PF}_6^-]$ to 83 °C for $[\text{hmim}^+][\text{PF}_6^-]$. The electroluminescent (EL) properties and the electronic structure of the LECs were characterized by current–voltage (I – V), light intensity–voltage (L – V), and ac impedance measurements. It was found that the phase compatibility between the conjugated polymer and the ionic liquid determines the performance of the light-emitting devices, and the concentration of the ionic liquid and the ionic conductivity of the polymer blend films also play an important role. The imidazolium salts investigated in this work are suitable for fabricating the LECs except for $[\text{bmim}^+][\text{PF}_6^-]$ which encounters phase separation problem with MEH–PPV. The LEC doped by $[\text{dmim}^+][\text{BF}_4^-]$ shows an EL external quantum efficiency of 0.2% at 4 V, which is comparable with that of the traditional LEC with PEO/ Li^+ salt as the polymer electrolyte. Room-temperature frozen p-i-n junction LEC was realized on the LECs based on MEH–PPV doped by $[\text{tmim}^+][\text{PF}_6^-]$ and $[\text{hmim}^+][\text{PF}_6^-]$ with the higher melting point. The frozen-junction LEC shows fast response, wide operating voltage window exceed 10 V and high EL performance. The external quantum efficiency of the LEC/ $[\text{hmim}^+][\text{PF}_6^-]$ achieved 1.4% at 10 V. The electrochemical doping mechanism of the LECs was confirmed by the ac impedance measurement of the devices. The ionic liquids are very stable and insensitive to humidity, which could enable the fabrication and characterization of the LEC outside a drybox.

1. Introduction

Polymer light-emitting materials and devices have drawn considerable attention since the discovery of the polymer light-emitting diode (PLED) in 1990.¹ PLED is usually composed of a luminescent polymer layer sandwiched between an ITO transparent anode and a low work function metal cathode. When a proper voltage is applied on the two electrodes, holes will inject from the anode and electrons will inject from the cathode into the HOMO and LUMO of the polymer, respectively. The injected holes and electrons move toward the inner part of the polymer layer, meet, and recombine to give out light. The effective injection of charges into the polymer active layer, which is crucial for the device performance, depends on the interfacial structures between the polymer layer and the electrodes of the devices.^{1–3} The interfacial structure, however, is always affected by the ionic impurities contained in the active polymer besides the intrinsic properties of the polymer and the work function of the electrode materials. It has been proved that the ionic impurities do play a very important role in both the properties of the conjugated polymer and the performance of the polymer optoelectronic devices.^{4–8} The conjugated polymers without specific purification usually show poor photoelectronic properties due to the charge trapping of impurities. The polymers for optoelectronic application, thereby, need to be purified carefully in the usual case.^{9–11}

However, the light-emitting devices may also benefit from the ions in the active polymer. The introduction of ionic species

into the polymer active layer on purpose enables the electrochemical doping of the polymer at the interface to occur^{12,13} or facilitates the formation of an ionic space charge layer at the interfaces,^{4,7,14,15} which is beneficial to the injection of holes/electrons into the device. The device based on the luminescent polymer blended with polymer electrolyte (PEO + Li^+ salt) is called a polymer light-emitting electrochemical cell (LEC) which is devised by Pei et al.^{12,13} The LEC is constructed with, just as that of the PLED, the anode of a ITO conducting glass, the cathode of a metal (Al, Au etc.), and the active polymer blend layer sandwiched between the anode and the cathode. The ionic dopants chosen for the devices must be highly stable with a large electrochemical stable potential window (ESPW), highly (photo)chemically inert, and dissociable in the solid film without any supporting solvents. The advantages of the LECs, in comparison with that of the PLEDs, are their low turn-on voltage benefited from the low resistance of the polymer layer and the easy injection of the charges, high electroluminescent efficiency due to the balanced electron/hole injection from the two electrodes, and high stability of the cathode because the inert metal can be used as the cathode in LECs instead of the low work function active metal used in PLED. However, there are some drawbacks with the LECs, such as phase separation between the nonpolar luminescent polymer and the polar polymer electrolyte, the limitation of the working voltage due to the electrochemical degradation (overoxidation, etc.) of the polymers and the electrolytes at higher voltages, the slow response due to the slow transportation of the ions in the

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polymer layer, and the sensitivity of the polymer electrolyte to humidity.

The phase separation in the LECs can cause the problems of poor performance and short lifetime of the devices. To achieve a high quality device, a surfactant was introduced to the active layer, which overcomes the phase separation problem a great deal and improved the response time of the LEC.¹⁶ However, the blend film with the surfactant is still humidity-sensitive. An ionic conducting side chain was also introduced into the conjugated polymer chain to obtain homogeneous bifunctional luminescent polymers,^{17–22} and the response characteristics were improved greatly for the bifunctional polymer LECs.^{23–25} However, the color of light emitted changed with operation, which may have resulted from a gradual phase transition of the polymers. No satisfactory way is found to solve the problems currently. The frozen-junction type LEC seems a desirable solution to a high quality LEC with fast response, high brightness (working voltage can reach as high as 15 V), etc.^{26–28} The frozen-junction LEC was obtained by cooling the pre-biased LEC to a temperature lower than the glass transition temperature of the ionic-conductive polymer, where the movement of ions was frozen and the as-formed p-i-n junction kept without relaxation. Therefore, the negative effect of ions in the active layer was restrained greatly. The disadvantage of the frozen-junction LECs, to date, is that the temperature that is needed for the frozen p-i-n junction is too low (lower than 200 K for the PEO type polymer electrolyte),²⁸ which is inconvenient for operation. Also, the problem of the sensitivity to humidity, which makes the fabrication have to be conducted in a glovebox, still remained.

Recently, an ionic liquid, also called as room temperature (RT) molten salt, has received much attention in the fields of organic synthesis, catalysis, and electrochemistry.^{29,30} The advantages of ionic liquids over inorganic salts are that they are soluble in most organic solution, insoluble in water (for the hydrophobic ionic liquid), dissociable to supply cations and anions, chemically and electrochemically stable at temperatures lower than 200 °C and within a large potential range, and almost nonvolatile. In addition, a high ionic conductivity of 0.1 S cm⁻¹ has been achieved according to the latest report for imidazolium salt.³¹ The higher ionic conductivity combined with the better stability promote the application of ionic liquids in electrochemical devices.^{32–34} Stephan et al. have used the ionic liquids of ammonium salts, which is a viscous liquid, in the LECs as the ionic carrier.^{35–37} However, a large amount of the salt was blended in the active polymer layer of the LECs, which may affect the stability of the LECs negatively. In this work, we introduce the ionic liquid of imidazolium salts into the LECs alternatively. The imidazolium salts could be synthesized and purified easily.^{38–40} The chemical structure as well as the polarity of the imidazolium salts are tunable with large diversity. Considering the requirement in the LEC fabrication, imidazolium salts are apparently superior over other inorganic and organic salts from the viewpoint of chemical tunability. In addition to the advantages mentioned above, these imidazolium salts can be blended with the conjugated polymer directly; no additional ionic-conducting polymer is needed in the fabrication of LEC devices. The frozen-junction type LECs were also fabricated successfully with the high-melting-point imidazolium derivatives salts.

2. Experimental Section

1-Methylimidazole and other chemicals were purchased from Acros. Imidazolium derivatives, 1-methyl-3-alkylimidazolium,

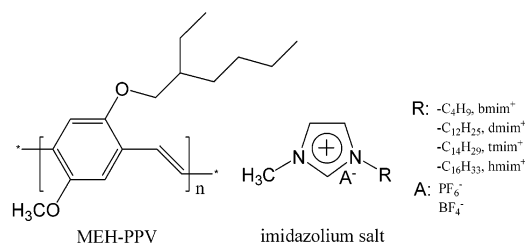


Figure 1. Chemical structure of MEH-PPV and imidazolium salts used in the experiments.

were synthesized with the reported method.^{38–42} 1-Methyl-3-alkylimidazolium hexafluorophosphates or tetrafluoroborates were prepared by metatheses from the corresponding chloride/bromide and recrystallized twice before use. Polymer light-emitting devices with a sandwich structure of ITO/polymer active layer/Al were fabricated in glovebox under N₂ atmosphere. Poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) was used as the luminescent polymer in the active layer. The chemical structures of MEH-PPV and the imidazolium derivatives salts used in this work are shown in Figure 1.

MEH-PPV was dissolved in cyclohexanone with a concentration of 10 mg/mL.⁴³ The ionic liquid (salt) was added into the MEH-PPV solution at the pre-defined content. The molar ratio of salt to polymer unit is varied from 1:10 to 1:120. The blend solution was spun-cast on a pre-cleaned ITO glass substrate at 2000 rpm. The thickness of the film is around 100 nm as monitored by an Ambios XP-2 step profiler (U.S.A.). The aluminum electrode was evaporated under vacuum, resulting in an active area of the LEC around 12 mm². The device structure could be written as ITO/MEH-PPV+salt/Al.

The current–voltage (I–V) and light intensity–voltage (L–V) characteristics of the light-emitting devices were recorded with a computer-controlled Advantest (Japan) R8340 Ultrahigh Resistance Meter and an Advantest R6551 Digital Multimeter coupled with a Si photomultiplier tube. Each point was recorded with a 2-s delay. A Zahner IM6e Electrochemical Workstation (Germany) was employed for impedance measurements and cyclic voltammetry on the LECs. The impedance measurements were performed with the frequency ranged from 100 Hz to 1 MHz and with an ac voltage amplitude of 20 mV under different biases. The scan rate of the cyclic voltammetry was 20 mV/s. The atomic force microscopy (AFM) was conducted on a Nanoscope III (DI, USA).

3. Results and Discussion

3.1. Properties of Imidazolium Salts. The polarity and melting point of the imidazolium derivatives salts (ImDS) can be regulated by changing their substituents at the N positions (1,3 positions) of the imidazole ring.^{29,39} For the purpose of fabricating room-temperature frozen p-i-n junction LEC with the imidazolium salt as the ionic source, we prepared various imidazolium derivatives salts with different substituents at the 3 position of the imidazole ring and different anions, which include 1-methyl-3-butylimidazolium hexafluorophosphate ([bmim⁺][PF₆⁻]), 1-methyl-3-dodecylimidazolium hexafluorophosphate ([dmim⁺][PF₆⁻]), 1-methyl-3-tetradecylimidazolium hexafluorophosphate ([tmim⁺][PF₆⁻]), 1-methyl-3-hexadecylimidazolium hexafluorophosphate ([hmim⁺][PF₆⁻]), [dmim⁺][BF₄⁻], [tmim⁺][BF₄⁻], and [hmim⁺][BF₄⁻]. The melting points of the ImDS are listed in Table 1. The lengthening of the alkyl chain at the 3 position of the imidazole ring raises the melting point of the ImDS and makes the polarity of the ImDS more

TABLE 1: Melting Points of the Ionic Liquids of the Imidazolium Derivatives Salts

ionic liquid	melting point/°C
[dmim ⁺][PF ₆ ⁻]	60
[dmim ⁺][BF ₄ ⁻]	34
[tmim ⁺][PF ₆ ⁻]	73
[tmim ⁺][BF ₄ ⁻]	38
[hmim ⁺][PF ₆ ⁻]	83
[hmim ⁺][BF ₄ ⁻]	46

hydrophobic. In addition, the anion in the salt also affects the melting point a great deal. The imidazolium salts with the smaller anion BF₄⁻ possess a lower melting point in comparison with that containing the larger anion PF₆⁻, see Table 1 for details.

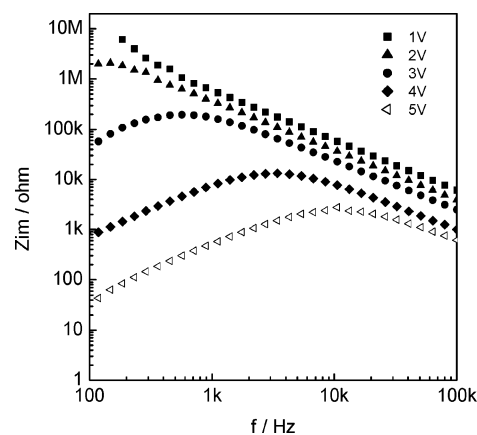
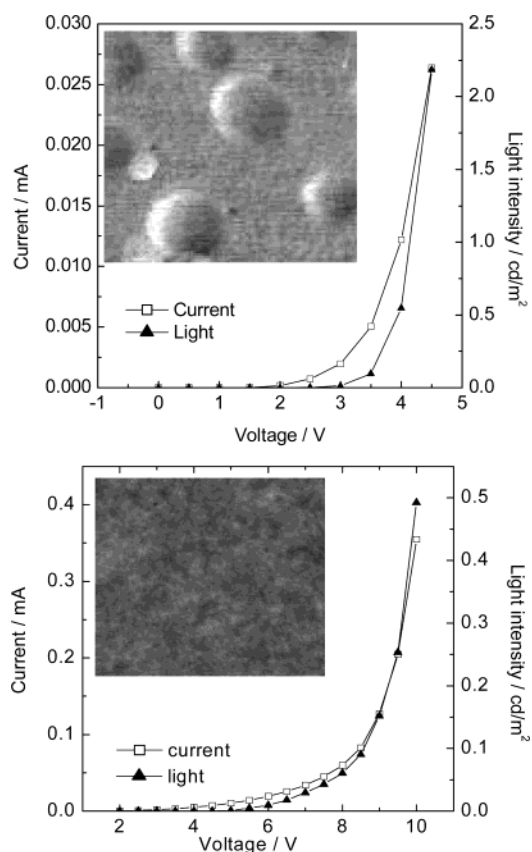
The polarity of the ionic liquid is crucial to the compatibility with the conjugated polymer. For the lithium salt used in the traditional LECs, PEO has to be used to “dissolve” the salt in the active blend film.

In the present studies, the polymer solvent PEO could be excluded because the polarity of the imidazolium salts is close to that of the conjugated polymers. The macroscopic phase separation could be avoided to a large extent. To check the effect of the polarity of the imidazolium salt on the film-forming property of the active polymer layer in the LECs, we also synthesized 1-methyl-3-tertbutylimidazolium hexafluorophosphate, which possesses a higher polarity than that of the ImDS mentioned above and is partially soluble in water. The ionic liquid was tried in the LEC fabrication. The LECs with this imidazolium salt tended to short due to the phase separation between MEH-PPV and the ionic liquid, and the lifetime of the devices was also quite limited. This indicates 1-methyl-3-tertbutylimidazolium is not suitable for the fabrication of the LEC without a PEO-like carrier because it is hydrophilic.

3.2. LEC Based on [bmim⁺][PF₆⁻]. [bmim⁺][PF₆⁻], which is in liquid state at room temperature, is hydrophobic, electrochemically stable within 4V and air/water insensitive.^{37,41} The polymer LEC based on MEH-PPV blended with [bmim⁺][PF₆⁻] was fabricated with the molar ratio of [bmim⁺][PF₆⁻] to MEH-PPV unit equal to 1:40. To study the electronic structure of the LEC, ac impedance was measured for the LEC at different bias voltages. The logarithmic plots of Z_{im} (imaginary part of the ac impedance) vs f (frequency), see Figure 2, show clearly the decrease of Z_{im} with the increase of voltage from 1 to 5 V, which indicates the increase of the device capacitance with the increase of the voltage.

From the linear part of the curves at high frequency, the capacitance can be calculated.⁴⁴ The results of the capacitance calculation are 2.44 nF at 1 V, 2.48 nF at 2 V, 2.58 nF at 3 V, and 2.76 nF at 4 V. The capacitance increases with voltage imply the occurrence of electrochemical doping in the LEC at the higher voltages, because the electrochemical doping makes the intrinsic layer of the polymer thinner so that the capacitance increased.^{44,45}

The I-V and L-V characteristics of the LEC are shown in Figure 3a. As seen in the figure, the turn-on voltage of the current is ca. 2 V, which is consistent with the value of the band gap of MEH-PPV, and the turn-on voltage for the light emission is 2.5 V. The turn-on voltage is dramatically decreased compared with that of the single-layered light-emitting diodes of ITO/MEH-PPV/Al (its turn-on voltage is about 12 V). No linear relationship was found between the injected current and the light emitted due probably to the complicated ions dissociation and the movement of the ionic liquid under the electric field.

**Figure 2.** ac impedance spectra of the LEC with [bmim⁺][PF₆⁻] (molar ratio of [bmim⁺][PF₆⁻]:MEH-PPV = 1:40).**Figure 3.** Current/light intensity/voltage curves of (a) the LEC/[bmim⁺][PF₆⁻] and (b) the LEC/[bmim⁺][PF₆⁻] with adding OCA. The insets show the corresponding phase images from AFM, and the size of the images is 2 μm × 2 μm.

The phase compatibility between MEH-PPV and [bmim⁺][PF₆⁻] was examined by AFM measurement of the polymer blend films (the AFM image is shown in the inset of Figure 3a). Spherical ionic liquid aggregates were observed within MEH-PPV on the scale of nanometers because of their polarity difference.

To improve the phase compatibility of [bmim⁺][PF₆⁻] with MEH-PPV, octylcyanoacetate (OCA), a nonionic surfactant,¹⁶ was added in the blend of [bmim⁺][PF₆⁻] and MEH-PPV for the fabrication of LECs. The AFM image, given in the inset of Figure 3b, shows the homogeneous morphology of the blend film with OCA. The results indicate that the addition of OCA improved the film-forming quality of the blend. However, the I-V and L-V performances of the device with OCA, as shown

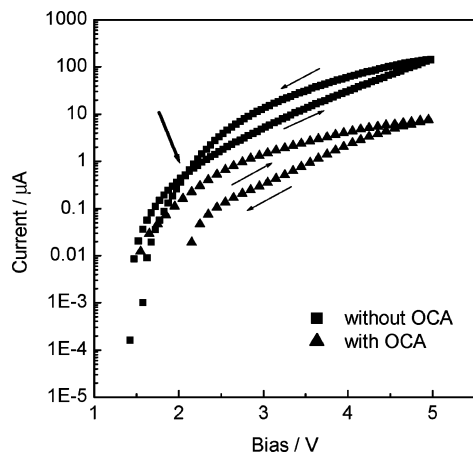


Figure 4. Cyclic voltammogram of the LECs(LEC/[bmim⁺][PF₆⁻]) with and without OCA. The scan rate is 20 mV/s.

in Figure 3b, turn worse in comparison with that of the device without OCA (see Figure 3a). The injection of current becomes difficult, and the turn-on voltage of light emission increases after adding OCA, which is contradictory to the result in the traditional LEC with PEO/Li⁺ as polymer electrolyte.¹⁶ Probably, the existence of OCA in the blend film of MEH-PPV/[bmim⁺][PF₆⁻] impeded the ionization and ionic transportation of the ionic liquids, and the addition of OCA diluted the concentration of the ionic liquid in the film, so that the ionic conductivity of the MEH-PPV/[bmim⁺][PF₆⁻] was decreased after adding OCA. The different nature of the ionic liquid and PEO/Li⁺ polymer electrolyte may result in the different effect of OCA on the ionic conductivity of the active layer of the LECs. Obviously, adding OCA is not an efficient way to improve the performance of the LEC/ionic liquid devices. Therefore, we tried other ImDS ionic liquids to solve the problem, which will be discussed in the latter parts of this paper.

The higher operating voltage (> 8 V) in Figure 3b is far beyond the electrochemical stable potential windows of the luminescent polymers.⁴⁶ The successful operation of the LEC at the higher voltage could be ascribed to the large electrochemical polarization that exists on the two electrodes due to the low concentration of the ions in the blend film. The electrochemical polarization also existed in the other LECs which could be operated beyond the voltage range of the electrochemical window of the luminescent polymers.

The results of cyclic voltammetry on the LEC/[bmim⁺][PF₆⁻], as shown in Figure 4, demonstrate the existence of a voltage threshold (around 2.0V) for electrochemical doping. The current of the LEC/[bmim⁺][PF₆⁻]/OCA is obviously lower than that of the LEC without adding OCA, which is coincident with the I-V and L-V results shown in Figure 3. The current hysteresis for the LEC/[bmim⁺][PF₆⁻] without adding OCA agrees with that observed by Greenwald et al.⁴⁶

The EL external quantum efficiency of the LEC/[bmim⁺][PF₆⁻] at 4.5 V is 0.04%. This quantum efficiency is 1 order of magnitude lower than that of the LEC with the PEO/Li⁺ salt polymer electrolyte but higher than that of the LEC based on ammonium molten salt.^{14,15} The ionic conductivity of the polymer active layer plays a very important role in the performance of the LECs. Higher ionic conductivity will improve the response time of the devices and the electrochemical doping of the conjugated polymer at the interfaces. The ionic conductivity of liquid [bmim⁺][PF₆⁻] (ca. 10⁻³ S cm⁻¹ at room temperature) is higher than that of the solid PEO/Li⁺ polymer electrolyte (ca. 10⁻⁴ S cm⁻¹ at room temperature),¹³ the diffusion

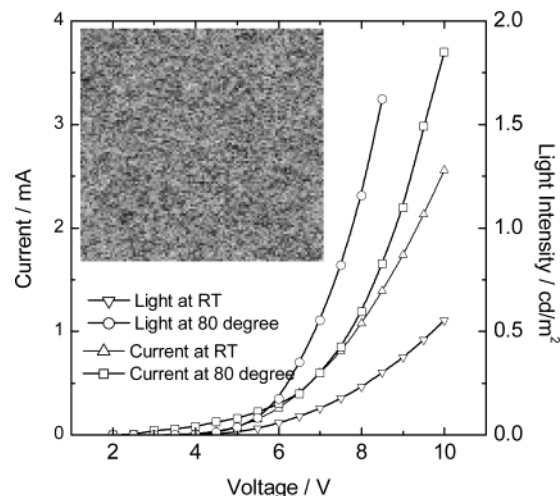


Figure 5. Current/light intensity/voltage curves of the LEC/[dmim⁺][PF₆⁻] (molar ratio of [dmim⁺][PF₆⁻]:MEH-PPV = 1:20) at RT and upon heating (80 °C). The inset shows the phase image from AFM, and the size of the image is 2 μm × 2 μm.

of counterions in polymer/[bmim⁺][PF₆⁻] blend should be more facile. However, the device quantum efficiency of polymer/[bmim⁺][PF₆⁻] is lower compared with the devices of polymer/PEO/Li⁺, as mentioned above. The lower current at the operating voltages indicates the poor doping of conjugated polymer in the LEC/[bmim⁺][PF₆⁻]. The phase separation between polymer and [bmim⁺][PF₆⁻] due to their polarity difference, as revealed by AFM, would cause the lower ionic conductivity of the polymer/[bmim⁺][PF₆⁻], which should be responsible for the lower quantum efficiency. Apparently, improving the polarity compatibility of the imidazolium salts with MEH-PPV should be very important to achieve a high performance LEC/imidazolium salt device.

3.3. LEC Based on [dmim⁺][PF₆⁻]. [dmim⁺][PF₆⁻] is soluble in most nonpolar organic solvents other than xylene and toluene, and this imidazolium salt is well compatible with MEH-PPV. The AFM observation reveals that the blend film of MEH-PPV and [dmim⁺][PF₆⁻] is homogeneous; no phase separation is found (see the inset of Figure 5). The melting point of [dmim⁺][PF₆⁻] is 60 °C, which indicates that operation temperature will affect the performance of the LEC/[dmim⁺][PF₆⁻] very much.

Figure 5 shows the effect of the operation temperature on the performance of the LEC/[dmim⁺][PF₆⁻]. The injection current and the light intensity at higher temperature are all increased greatly compared with that at RT because the melted [dmim⁺][PF₆⁻] salts at higher temperature improve the electrochemical doping and the efficiency of the devices. This is also confirmed by the ac impedance measurement,^{44,45,47} as shown in Figure 6. The total impedance of the LEC at both RT and 80 °C decreases with the increase of the bias voltage, the impedance at 5 V decreases 70% compared with that at 0 V for the LEC at RT, whereas the impedance at 3 V decreases 85% compared with that at 0 V for the LEC at 80 °C. This also indicates that a higher temperature promotes the dissociation of [dmim⁺][PF₆⁻] and the doping. However, it can be noted that the injection current is relatively low at lower biases at both RT and 80 °C. It means that the doping in the device is not very efficient at lower biases compared with the conventional LEC with PEO/Li⁺ salt. No steady state is achieved in such LECs.

The content of [dmim⁺][PF₆⁻] in the active layer of the LEC/[dmim⁺][PF₆⁻] also affects the performance of the LEC, because

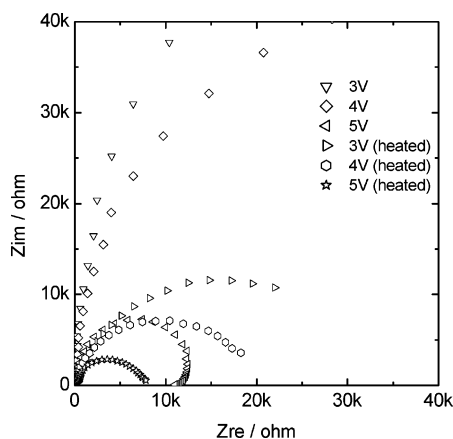


Figure 6. Nyquist plot of the ac impedance of the LEC/[dmim⁺][PF₆⁻] (molar ratio of [dmim⁺][PF₆⁻]: MEH-PPV = 1:20) with (at 80 °C) and without heating.

the concentration change of the ImDS will influence the microscopic morphology and ionic conductivity of the active layer. The content of the salt in the active layer must be optimized. Too less content of the salt will lead to poor electrochemical doping at the interfaces. While too much content of the salt could screen the electric field, affect the response time of the LEC negatively, though the turn-on voltage of the LEC could be decreased. For example, when the molar ratio of [dmim⁺][PF₆⁻] to polymer unit is 1:20, the corresponding LEC/[dmim⁺][PF₆⁻] turns on at 3 V, whereas with the ratio of 1:40, the turn-on voltage increases to 6 V (which is still lower than that of the LED with the same structure).

For all of the LECs with the content of [dmim⁺][PF₆⁻] equal to or less than 1:20 (molar ratio of the salt to MEH-PPV unit), the I-V and L-V curves under positive voltage and negative voltage are not symmetric as conventional LEC. This can be ascribed to the low content of the supporting salt in the active layer as pointed out by de Mello et al.^{15,48}

The LEC/[dmim⁺][PF₆⁻] with a molar ratio of 1:20 also shows the slow response behavior at RT due to lower ionic conductivity. When a bias above the turn-on voltage is applied, the device lights at one spot at the beginning, and then the light-emitting area spreads to the whole active area. After the first operation, that is, after a pre-biased treatment, the performance of the LEC can be improved in the afterward operation. The turn-on voltage of the LEC after the pretreatment can decrease to 2.5–3 V. The pre-biased LEC also shows higher light intensity than that of the device without the pre-biased treatment.

The nature of the anion in the imidazolium salt affects the polarity as well as the melting point of the ionic liquid.²⁹ The ImDS with [BF₄⁻] as anion shows a lower melting point, as shown in Table 1. The LEC doped with [dmim⁺][BF₄⁻] was also fabricated and characterized, and the I-V and L-V curves are shown in Figure 7. It can be seen that the [dmim⁺][BF₄⁻] doped LEC shows much better performance than [dmim⁺][PF₆⁻] doped one at room temperature. The relatively lower melting point of [dmim⁺][BF₄⁻], 34 °C, which is comparable with the environment temperature, should be responsible for this improvement. The LECs of MEH-PPV/[dmim⁺][BF₄⁻] gave external quantum efficiency of 0.2% at 4V.

3.4. Room-Temperature Quasifrozen p-i-n Junction LEC Based on the Imidazolium Salts. [tmim⁺][PF₆⁻] and [hmim⁺][PF₆⁻] are soluble in any nonpolar organic solvents, which expands the variety of possible solvents in preparing the polymer solutions. For [tmim⁺][PF₆⁻] and [hmim⁺][PF₆⁻], it was found

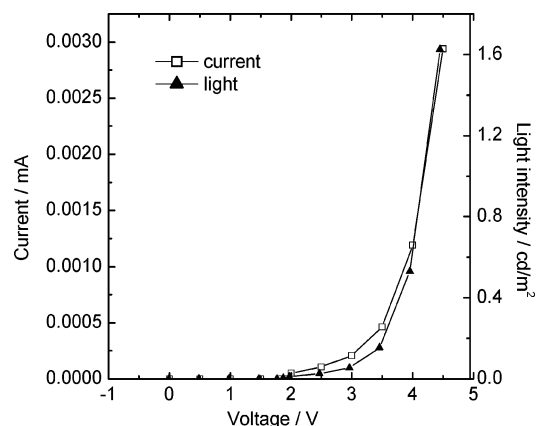


Figure 7. Current/light intensity/voltage curves of the LEC/[dmim⁺][BF₄⁻] ((molar ratio of [dmim⁺][BF₄⁻]: MEH-PPV = 1:60).

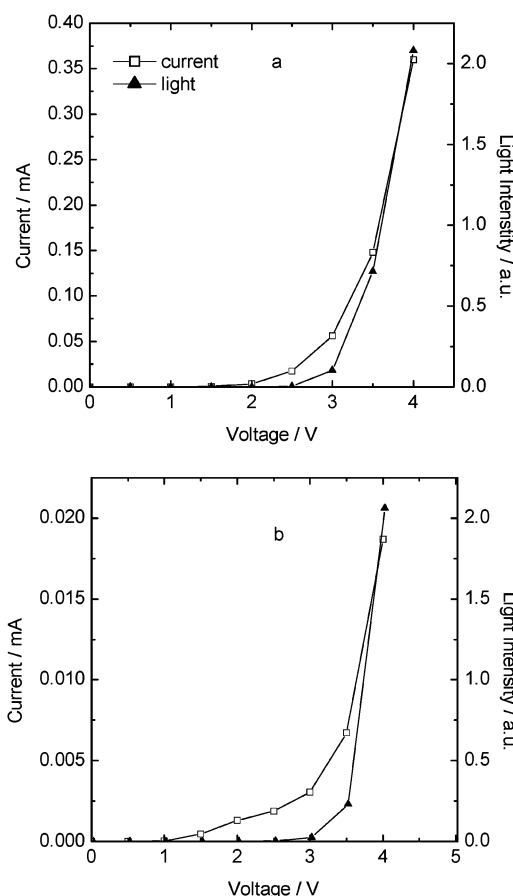


Figure 8. Current/light intensity/voltage curves of the LEC/[tmim⁺][PF₆⁻] (1:40) (a) and [hmim⁺][PF₆⁻] (1:80) (b) under heating (at 90 °C).

that the content of salt needed in the active layer is much less than that with [dmim⁺][PF₆⁻]. The LEC with a ratio of 1:40 ([tmim⁺][PF₆⁻]:MEH-PPV unit) gives off light at about 2.2 V upon heating to 90 °C (see Figure 8a), whereas the LEC with a ratio of 1:80 of [hmim⁺][PF₆⁻] to polymer unit also gives off light at ca. 2.2 V (see Figure 8b) under the condition of heating to 90 °C. It should be noted that 2.2 V of light-on voltage is equal to the band gap value of the MEH-PPV, which is one of the characteristics of the LECs.¹⁴ This indicates that the devices with such a content of salt are electrochemically operated. The heated temperature of 90 °C is higher than the melting point of the imidazolium salts of [tmim⁺][PF₆⁻] and [hmim⁺][PF₆⁻] (see Table 1). Hence, the heating turned the blend film into the high

ionic-conducting phase, which improves the performance of the LECs.

The unheated devices showed higher turn-on voltage around 4 V. If a higher content of imidazolium salt was used in the active layers, the resulting LECs gave off light at 2.0 V or lower, but the operating window was limited with 4 V, otherwise the devices degraded. Moreover, the devices showed severe relaxation behavior: the turn-on voltage shifted to lower values with the continuous voltage scan, whereas the current increased with the scan. The compatibility of salt and polymer is responsible for the good-performance of the devices obviously. Because $[\text{hmim}^+][\text{PF}_6^-]$ with a long alkyl chain at the imidazole ring is more compatible with the polymer, the corresponding LECs show better performance (the average efficiency is around 1%) compared with other imidazolium salts doped LECs.

The LECs with $[\text{tmim}^+][\text{BF}_4^-]$ and $[\text{hmim}^+][\text{BF}_4^-]$ as the ionic source were also studied. The LEC/ $[\text{tmim}^+][\text{BF}_4^-]$ showed dissatisfactory performance compared with that of the LEC/ $[\text{tmim}^+][\text{PF}_6^-]$. The LEC/ $[\text{hmim}^+][\text{BF}_4^-]$ showed severe relaxation behavior; no steady state could be observed, and the light-emitting efficiency was not good enough. The detailed mechanism for this difference is still unclear.

Because the ionic liquids can be heated to melt at a relatively low temperature, it is expected to fabricate the frozen-junction type LECs with such ionic liquids.^{26,27} First, the frozen LECs were made with heating the LEC/ $[\text{dmim}^+][\text{PF}_6^-]$ to 70 °C with bias on, and then the devices were frozen quickly to RT. Figure 9a shows that the frozen LEC turns on at a lower voltage, and the corresponding injection current is lower compared with the heated one (see. Figure 5), which could be attributed to the elimination of charging current or resulted from insufficient doping during the treatment. If the driving bias is higher than 10 V, the device tends to degrade. In fact, this LEC/ $[\text{dmim}^+][\text{PF}_6^-]$ is not a real frozen-junction device, because the junction will relax gradually at RT if the device was kept at biases lower than the turn-on voltage.

The joule heat from IR for a working device is unavoidable due to the intrinsic resistance of the light-emitting devices; hence, the light-emitting devices always work at a temperature higher than RT.⁴⁹ For the LEC with a frozen-junction formed, the ions may move again during operation due to the temperature increase, so that the frozen-junction might be ruined. This means that the ionic liquids used for the frozen-junction LEC should be those with higher melting points. The ionic liquids of $[\text{tmim}^+][\text{PF}_6^-]$ (MP = 73 °C) and $[\text{hmim}^+][\text{PF}_6^-]$ (MP = 83 °C) seem more suitable for fabricating the frozen-junction LECs. Figure 9, parts b and c, presents the results of the frozen-junction LECs with these two salts. It is found that the frozen-junction LEC/ $[\text{hmim}^+][\text{PF}_6^-]$ showed the better performance than that of the frozen-junction LEC/ $[\text{tmim}^+][\text{PF}_6^-]$. Although the melting points of $[\text{tmim}^+][\text{PF}_6^-]$ are suitable to some degree, the I–V and L–V curves show the nonlinear relationship between current and light intensity, which means that the movement of ions is not totally suppressed at RT. The frozen p–i–n junction of LEC/ $[\text{tmim}^+][\text{PF}_6^-]$ relaxed to some extent during the operation.

For a frozen-junction LEC, besides the DC characteristics mentioned above, the ac impedance spectra, as given in Figure 10, show clearly the difference from the normal LEC (see Figures 2 and 6). In Figure 10, each curve of the ac impedance at different voltages is a standard semicircle, and there is no capacitance change at different biases. A standard RC equivalent circuit simulates the impedance spectra very well, which is a characteristic of PLED.⁵⁰ The frozen-junction LEC worked in

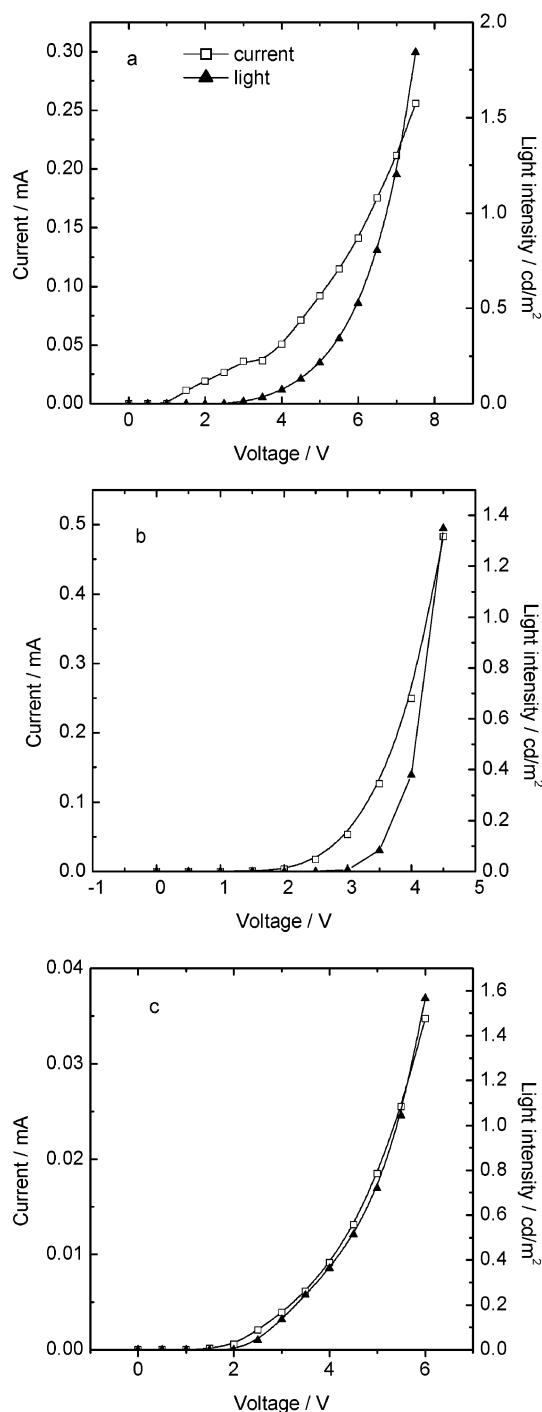


Figure 9. Current/light intensity/voltage curves of the frozen-junction LECs: (a) LEC/ $[\text{dmim}^+][\text{PF}_6^-]$; (b) LEC/ $[\text{tmim}^+][\text{PF}_6^-]$; (c) LEC/ $[\text{hmim}^+][\text{PF}_6^-]$.

the same way as the PLEDs. Thereby, the flattened semicircles in the Nyquist plot of the LEC (see Figures 2 and 6) should be reasonably attributed to the movement of free ions presented in the active layer under ac perturbation rather than to other reasons.^{44,45}

Comparison of the impedance spectra, shown in Figure 11, indicates that both pre-bias and heating are important for the successful preparation of the frozen-junction LEC. The diameter of the semicircles in Figure 11 indicates the total resistance of the devices at the operation voltage, and a lower value of the resistance reflects a larger amount of charges injected and usually a better performance of the devices. The resistance at 5 V is 14.0 kΩ for the as-prepared LEC, 10.0 kΩ for the 10

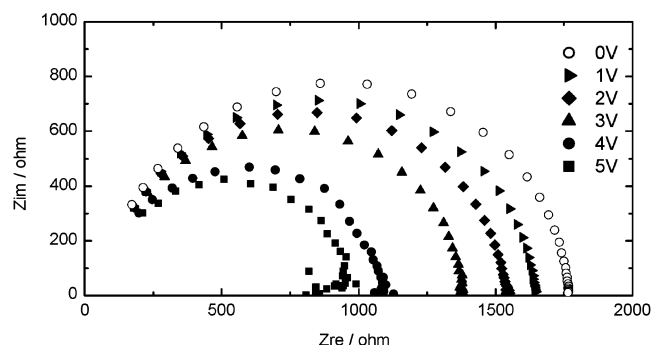


Figure 10. ac impedance spectra of the frozen-junction LEC/[hmim⁺][PF₆⁻] at various voltages.

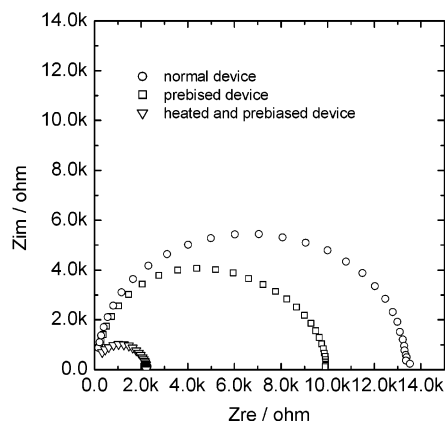


Figure 11. Nyquist plot of the ac impedance of the polymer LEC/[hmim⁺][PF₆⁻] at 5 V and at room temperature. The LECs are as-prepared (circle), prebiased at 10 V (square), and prebiased at 7 V under 90 °C (triangle).

V-prebiased LEC, and 2.0 kΩ for the LEC prebiased at 7 V under 90 °C. The lower resistance for the prebiased devices should be related to the p-i-n junction structure of the LECs formed by the electrochemical doping of the conjugated polymer during the prebiased treatment. Obviously, the heating to melt the ionic liquid increases the concentration of the free ions in the active layer of the LEC and the ionic conductivity of the active layer, which benefits the doping at the interfaces and ensures the frozen p-i-n junction LEC to be operated. Though LEC/[hmim⁺][PF₆⁻] gives satisfactory behavior of the frozen-junction LEC, the quantum efficiency at lower voltages is not very high yet, about 0.2%. The LEC/[hmim⁺][PF₆⁻] operated at 10 V reaches its highest quantum efficiency of 1.4%. The efficiency is related to the current injected into the active layer. As seen from Figure 8, the device shows a relatively low injection current at low voltage. If the charge injection at low voltage could be improved, the light-emitting efficiency would be increased further.

The results of the LECs based on the ImDS ionic liquids indicate that the length of the alkyl substituents on the 3 position of the imidazole ring plays a very important role on the performance of the LECs. The effects are mainly related to the compatibility (polarity) of the ImDS with MEH-PPV, the melting point of the ImDS, and the ionic conductivity of the MEH-PPV/ImDS blend films. Compatibility is the most important factor. Hence, [dmim⁺][PF₆⁻], [tmim⁺][PF₆⁻], and [hmim⁺][PF₆⁻] are suitable for fabricating LECs with MEH-PPV, whereas [bmim⁺][PF₆⁻] is not suitable because of the phase separation between [bmim⁺][PF₆⁻] and MEH-PPV. Ionic conductivity is another important factor for the effective electrochemical doping and fast response of the LEC. From this viewpoint, [dmim⁺][BF₄⁻] is a good ionic liquid for the

fabrication of LEC with MEH-PPV. Although for a frozen-junction LEC, the melting point of the ionic liquid plays an important role, which will be discussed in the following.

For the high melting point [hmim⁺][PF₆⁻] (melting point is 83 °C), the content in the active layer must be optimized. In the process of frozen-junction LEC fabrication, once the doping layers formed at the interface, the free ion/salt in the intrinsic layer should be as little as possible so that the devices could keep their steady state under bias. That is the reason frozen-junction LEC/[hmim⁺][PF₆⁻] gave the best result (see Figure 9c). The ionic conductivity is no longer important for a frozen LEC, but the melting point of the ionic liquid is crucial. From the point of application, the limited content of salt is favorable, because the criteria of the column-row display includes unipolar, switch-like I-V to avoid cross talk, which is possible only in the LECs with lower content of salts. The LECs doped with the high-melting-point [hmim⁺][PF₆⁻] show promising results. A successful frozen-junction LEC should give a linear relationship between current and light intensity and a semicircular response in the Nyquist plot of AC impedance. There will be no effect of ions existed in the devices.

Finally, it should be pointed out that the melting point of the ionic liquid of [hmim⁺][PF₆⁻] is still somewhat lower. The melting point around 100 °C would be ideal, considering the practical application of the room-temperature frozen p-i-n junction LECs.

4. Conclusions

The ionic liquids of 1-metal-3-alkylimidazolium salts with different alkyl substituents were blended with MEH-PPV to fabricate polymer LECs, and the performance of the LECs were characterized by I-V, L-V, and ac impedance measurements. The effect of the length of the alkyl substituents was investigated. The results can be concluded as follows.

The compatibility of the ionic liquids with MEH-PPV is related to the nature of the alkyl substituents in the 3 position of the imidazole ring. When the alkyl is dodecyl, tetradecyl, or hexadecyl, the compatibility of the ionic liquid with MEH-PPV is very good. Although, when the alkyl is butyl, there is a phase separation problem in the MEH-PPV/ionic liquid blend. The difference of the compatibility comes from their difference in polarity of the ionic liquids with different alkyl substituents.

The concentration of the ionic liquid affects the performance of the light-emitting devices. A higher concentration of salts in the film results in a nonlinear relationship between the injected current and the light emitted, and the electrochemical steady-state cannot be established if the salt concentration is too high. The appropriate content of salt ensures the high performance of the LECs.

Room-temperature frozen p-i-n junction LEC can be achieved from the LEC doped with the higher melting point [hmim⁺][PF₆⁻]. The compatibility with the luminescent polymer and the higher melting point of the ionic liquid are crucial for the fabrication of the frozen-junction LEC.

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