Reverse bias activation of salt-doped polymer light-emitting devices

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ABSTRACT

We report sandwich polymer light-emitting devices doped with a lithium salt. The salt-doped polymer devices are initially conductive and weakly emitting under forward bias but blocking under reverse bias. The application of a large reverse bias or current activates the device, causing a dramatic increase in current and the onset of electroluminescence under reverse bias. Meanwhile, the forward-bias current and emission have become heavily suppressed. Moreover, the activated devices exhibit photovoltaic response whose polarity is opposite to that of an un-activated device. Electrical, electroluminescent, photoluminescent and photovoltaic properties of the activated devices suggest the formation of a p–n junction by *in situ* electrochemical doping. Devices made with a green-emitting polymer are quasi-frozen with no significant degradation in current density and light intensity after 1200 h of storage at room temperature.

1. Introduction

The light-emitting electrochemical cell (LEC) has been investigated in the last two decades for its interesting electrical and optical properties, as well as its potential lighting and display applications [1–10]. LECs are unique among organic devices due to their operating mechanism, which is that of *in situ* electrochemical doping and junction formation [11–13]. Key to the doping process is the availability of mobile ions in the active layer, which serves to stabilize/neutralize the injected electronic charges when the luminescent polymer is reduced or oxidized. The mobile ions are provided by a solid electrolyte, typically consisting of an ion-solvating/transport material and a salt. The active layer of an LEC is therefore a mixed ionic/electronic conductor in the form of an interpenetration network [14]. *In situ* electrochemical p- and n-doping of the luminescent polymer occur when a voltage bias larger than E_g/e is applied, where E_g is the energy gap of the luminescence polymer and e is the elementary charge [15]. A polymer p–n junction is eventually formed and light emission occurs via the injection of minority charge carriers across the p–n junction.

Unless the luminescent polymer is itself an ion conductor or the salt used is an ionic liquid (molten salt) [16–20], the active layer of

a polymer LEC typically consists of three components: a luminescent polymer, an ion-solvating/transport polymer, and a salt [10,11]. The most commonly used ion solvating/transport polymer is polyethylene oxide, or PEO, which functions as a dry solvent for alkali salts such as lithium triflate by forming complexes with the salt cation. In the MEH-PPV:PEO:LiTf composite both cations and anions are mobile, and the ion profiles have been determined [7]. With polymer LECs in an extremely large planar configuration, the dynamic doping and junction formation processes can be visualized by fluorescence imaging [21–23]. Such large planar devices, however, invariably require a large amount of electrolyte typically accounting for over 50 wt% of the blend in order to achieve sufficient ionic conductivity and doping [13,21,22,24]. In sandwich LECs, the electrolyte amount can be much lower and low electrolyte loading has been an effective approach to achieve long-lasting devices [25,26]. It is still unexpected, however, to discover that polymer LECs, with the PEO component completely absent, could still be activated to emit and conduct strongly [27].

Unlike conventional polymer LECs, these two-component, salt-doped polymer LECs require an activation voltage much higher than E_g/e and the "turn-on" is abrupt [27]. Similar device activation behaviours have also been reported in multi-component, molecule-dispersed polymer light-emitting devices consisting of a wide energy gap polymer host, a small molecule fluorescent or phosphorescent emitter, an electron-transport material and a solid salt [28–33]. It was believed that the host polymer had been electrochemically p- and n-doped [29]. Our salt-doped polymer devices

offered first evidence of such doping. Moreover, we observed that the activated, or doped device was quasi-static and lasted about 150 h. The activated devices, however, did not emit uniformly with interesting formation of concentric rings [27].

In this study, we report salt-doped polymer light-emitting devices activated by a reverse bias. The activation process reverses the polarity of the devices as they become conductive and emitting when the ITO electrode is biased negatively relative to the aluminium electrode. Photovoltaic measurements confirm that the built-in field of the devices has also been reversed. The light emission is uniform and absent of any ring formation. Moreover, the devices made with a green-emitting polymer are stable for over 1000 h after activation. We discuss the results in the context of doping and frozen-junction LECs.

2. Experiment

We used two luminescent polymers in this study: poly[5-(2′-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene], MEH-PPV, an orange-emitting polymer sourced from OLED King Ltd, China with $M_w = 3.3 \times 10^5$ and a polydispersity index of 1.4, and poly[(9,9-dioctyl-2,7-divinylene-fluorenylene)-alt-co-{2-methoxy-5-(2-ethyl-hexyloxy)-1,4phenylene}], ADS108GE, a co-polymer synthetized by American Dye Source with $M_w = 30,000–50,000$. The salt used was lithium trifluoromethanesulfonate (LiTf). Polymers and salt alike were dissolved separately in cyclohexanone and subsequently mixed to create two solutions: one containing 10 mg of MEH-PPV and 1 mg of LiTf per 1.08 ml of solvent and the second containing 10 mg of ADS108GE and 1 mg of LiTf per 1.08 ml of solvent. The solutions were spin cast onto pre-patterned ITO glass substrates and heated for 5 h at 50 °C to dry the polymer films. The salt-containing polymer films were optically clear and indistinguishable in appearance from pure polymer films. The thickness of the polymer films was measured with an Ambios optical profiler. The MEH-PPV:LiTf film had a thickness of 200 ± 6 nm and the ADS108GE:LiTf film had a thickness of 127 ± 7 nm. The ITO glass substrates were cleaned in acetone and isopropanol under ultrasonication and treated in an UV-ozone chamber before use. Finally, high purity aluminium (>99.99%) was thermally evaporated onto the polymer film through a shadow mask to form the top electrode 100 nm thick. The top aluminium electrode defined the active area of the device as 0.116 cm^2. Except for the weighing of dry materials, the entire device processing and testing procedures were carried out in a nitrogen-filled glove box/evaporator system.

The finished devices were mounted in a black box fitted with a silicon photodiode and electrical feed-through. A computer controlled Keithley 238 source measurement unit powered the devices while simultaneously measuring the device current or voltage. The device luminance was measured with a photodiode calibrated by a Minolta LS-110 luminance meter. For photovoltaic measurements the black box lid was removed and the devices were exposed to 100 mW/cm^2 AM1.5 illumination from a solar simulator through the glove box window. The illumination power was measured using a Thorlabs power meter with a broad-spectrum thermopile detector. All tests were conducted at an ambient temperature of 26 °C.

3. Results

The salt-doped devices were turned on, or activated by applying either a constant voltage or current with the ITO electrode biased negatively relative to the aluminium electrode. In the case of constant voltage activation, a constant reverse bias was applied for 60 s and ramped up if the device was still not activated. The voltage increase/60 s wait cycle was repeated until a sudden rise in device

current and luminance was observed. The applied voltage bias was then promptly removed in order to prevent damage to the device. Alternatively, the device was activated by applying a large reverse current. Since the device was initially highly resistive under a reverse bias, the applied current forced a large reverse bias that caused fast activation of the device. Subsequently, the applied bias was automatically lowered by the Labview test problem in order to maintain the applied current. The constant-current activation is therefore self-limiting and less likely to cause device damage due to high power input. The activation of a MEH-PPV device was captured in video and included in the Supplemental Information. A −50 mA constant current was applied to the device. We observe that the emission initially only occurred in parts of the device but quickly spread to the entire device and became stronger with time.

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.orgel.2015.10.005.

The activation process drastically altered the device current and luminance. Fig. 1 compares the current density/luminance vs. voltage bias (J–L–V) characteristics of a MEH-PPV:LiTf device before and after a −40 mA constant current was applied. The voltage bias was scanned from 0 to −15.5 V. The pristine device initially behaved like a reverse-biased polymer light-emitting diode. Because of the large charge injection barriers for both electrodes and holes under reverse bias, the device was highly resistive and not light emitting. After activation, however, the same device displayed luminance over 100 cd/m^2 at −15.5 V. And the current density reached over 150 mA/cm^2 at the same voltage. The low threshold for electroluminescence of −3 V, as determined from the luminance vs. voltage data in semi-log form, suggests that the activation process has fundamentally altered the nature of the device.

The activation behaviour was not unique to devices based on MEH-PPV. Fig. 2a shows the J–L–V characteristics of the ADS108GE device before and after a −40 mA constant current was applied. We observe that after activation the devices again exhibit pronounced current density and luminance, although both were smaller than the MEH-PPV devices. We also note that the current density exhibit a high and broad peak centred at around −4 V. This "negative differential resistance" behaviour has been widely reported in organic and polymer LEDs [34–38]. Since the high current density was not accompanied by light emission, it was mostly likely due to a tunnelling leakage current. Under forward bias, the green-emitting device was initially highly conductive, as shown in Fig. 2b. At +3.8 V, the current density reached 466 mA/cm^2 and the device
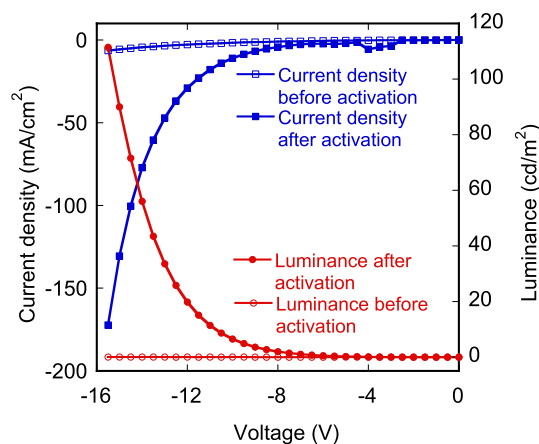

Fig. 1. Current density/luminance vs. voltage bias (J–L–V) characteristics of an ITO/MEH-PPV:LiTf (10:1)/Al device before and after a −40 mA constant current was applied at room temperature.