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Use of ionomer as an electron injecting and hole blocking material for polymer light-emitting diode

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Light-emitting diodes of poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) are fabricated using sodium sulfonated polystyrene (SSPS) ionomer containing 10 mol % ionic groups as an electron injecting and hole blocking material. When an electric field stronger than 2.7×10^7 V/m is applied, SSPS in the indium-tin oxide ITO/MEH-PPV/SSPS/Al system causes a bridging effect between sodium ions and the Al cathode at the SSPS/Al interface, leading to excellent electron injection. Furthermore, the ionomer has a high band gap energy of ~ 5 eV, resulting in hole blocking. The operating voltage for the ITO/MEH-PPV/SSPS/Al is reduced by $\sim 60\%$ and the relative quantum efficiency is enhanced by three orders of magnitude compared with those of the corresponding single-layer MEH-PPV device. © 1998 American Institute of Physics. [S0003-6951(98)03319-1]

Polymer electroluminescence (EL) devices have been developed for the application in thin film displays in the last several years.¹⁻³ To achieve a highly quantum efficient EL device, injection of the holes and the electrons and transport in the emissive layer should be balanced to recombine efficiently. Unfortunately, most of the emissive polymers have low electron affinity, causing hole transport to dominate. It is well known that there are two options to solve the problem: one could use a cathode with a low work function such as Li, Ca, and Mg,⁴ or introduce a novel electron transporting material with a high electron affinity. As far as the stability of the device is concerned, the latter option is more practical. Recently, poly(phenyl quinoxaline) (PPQ) which is thermally stable and has a high electron affinity, has been used as an electron injecting and hole blocking material.^{5,6}

In this letter, an ionomer is used as an electron injecting and hole blocking material in the EL devices. Ionomers are thermoplastic resins that contain metal ions as well as the organic ionic molecules as the pendant group in the polymer chain.⁷ These ions in the polymer, which can be doped with many kinds of metal ions such as Na^+ , Li^+ , Cu^{++} , and Al^{+++} , can play a role as the reversible cross-linking sites resulting in good thermal and mechanical properties while maintaining thermoplastic processibility. It is expected that the metal ions in ionomers be compatible with the metal cathode, leading to good electron injection. Because of the large difference in the dielectric properties between the ionic and the hydrocarbon phases, a peculiar morphology in the aggregation of the ionic groups in ionomers is favored.⁸

In general, the multiplet defined as the primary aggregate of the ionic group is the starting point for describing the morphology.⁹ All the ionic groups are gathered inside to form the multiplet while the polymer chains are arranged

outside the multiplet. The polymer chains attached to the multiplet will be constrained in their mobility. This constraint is due to the multiplet, regarded as a relatively immobile rigid body with a high molecular weight, as well as to the highly crowded polymer chains in the vicinity of the multiplets.¹⁰ The multiplet, which is an aggregate of ionic groups surrounded by a polymer with reduced mobility, has a diameter on the order of 30 \AA .¹¹

Polystyrene with a molecular weight of 80 000 g/mol and molecular weight distribution of 1.08 is prepared through anionic polymerization using an appropriate amount of *n*-butyl lithium as an initiator. Then, a sodium sulfonated polystyrene ionomer containing 10 mol % ionic groups is prepared by sulfonation of the polystyrene in ethylene dichloride using acetyl sulfate as a sulfonation agent. Ion contents in the polymer are controlled by the amount of acetyl sulfate added during the sulfonation reaction. Details of the preparation have been described elsewhere.¹² The chemical structure of sodium sulfonated polystyrene (SSPS) and its aggregated form are shown in Fig. 1. Four different polymer light-emitting devices of poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) are fabricated on indium-tin oxide (ITO) coated glass substrates; a single layer structure device of (i) ITO/MEH-PPV/Al, and three two-layer structure devices of (ii) ITO/MEH-PPV/SSPS/Al, (iii) ITO/SSPS/MEH-PPV/Al, and (iv) ITO/MEH-PPV/SSPS/Au. Thicknesses of MEH-PPV and SSPS are 60 and 15 nm which are obtained by averaging the several measurements, respectively. Al (100 nm thick) and Au (80 nm thick) cathodes are evaporated *in vacuo* at a pressure of about 10^{-6} Pa.

In order to figure out the role of the SSPS ionomer layer in the device, current-voltage (*I-V*) characteristics of all the devices are measured and shown in Fig. 2. Previous work on the MEH-PPV single layer device has identified the hole as the major carrier.¹³ It is seen that the ITO/MEH-PPV/

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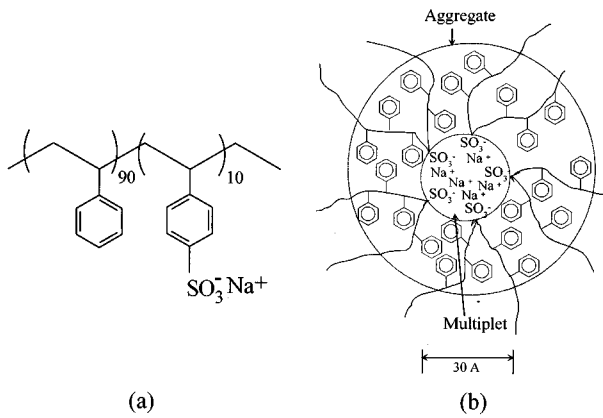


FIG. 1. The chemical structure of the ionomer used in this study (a) and its aggregated form (b).

SSPS/Al device is turned on at a lower field compared with the corresponding MEH-PPV single layer device. The rectification ratio at 4 V is found to be $\sim 5 \times 10^5$. The threshold voltage of the ITO/MEH-PPV/SSPS/Al device for turn on is about 2 V as seen in the inset of Fig. 3. When we replace the relatively low work function of an Al cathode (4.3 eV) by the higher work function of Au (5.2 eV), there would be much less current flow in that device leading to no light emission if SSPS worked only as a higher energy barrier. However, it is found that the ITO/MEH-PPV/SSPS/Au device has more current flow than the ITO/MEH-PPV/Al device under the same applied electric field and emits light, even though no light emission in the ITO/MEH-PPV/Au device could be detected. These results indicate that the ionomer does indeed lead to more efficient electron injection. On the other hand, it should be noted that the apparent electric field for the same current injection in ITO/SSPS/MEH-PPV/Al device is higher than any other devices, as seen in Fig. 2.

Variations of the optical power versus the electric field for three devices are presented in Fig. 3. The inset shows the enlarged portion of low luminescence versus applied voltage

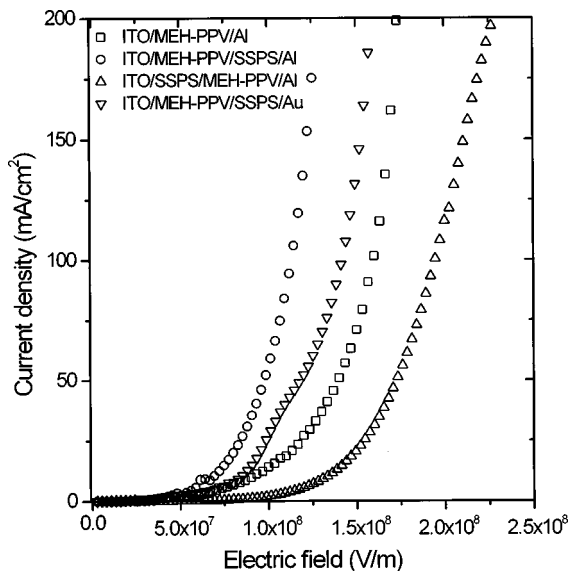


FIG. 2. Current density vs electric field characteristics of the devices with ionomers.

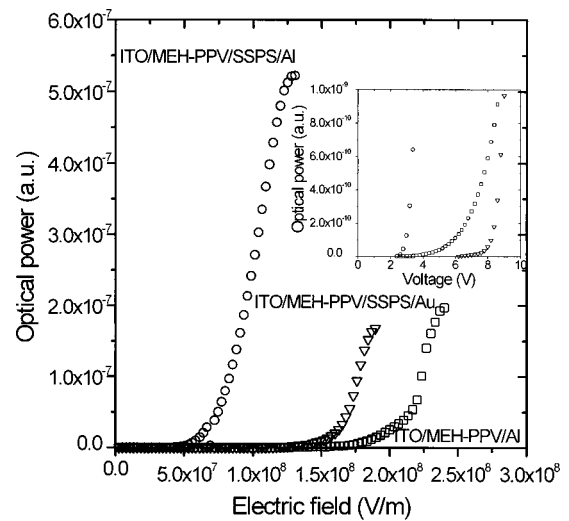


FIG. 3. Optical power vs electric field characteristics for the devices with ionomers. The inset shows the optical power operated voltage characteristics for the corresponding devices.

characteristic curves. Threshold voltage for the detection of light emission is as low as ~ 2 V for the ITO/MEH-PPV/SSPS/Al device, which is reduced by $\sim 60\%$ compared with the ITO/MEH-PPV/Al. As seen in the inset, the light output from ITO/MEH-PPV/SSPS/Al increases very sharply as the voltage increases, while the single-layer MEH-PPV device shows a slow rise. The light emission from the ITO/MEH-PPV/SSPS/Al is approximately 1000 and 100 times more efficient at low (~ 5 mA/cm²) and high (~ 200 mA/cm²) current densities, respectively, than from the single layer MEH-PPV device (see Fig. 4). Optical power of the ITO/MEH-PPV/SSPS/Al is much higher in the entire range of current density than the other devices. Based on the behavior demonstrated above, it is obvious that SSPS dramatically improves the device behavior and performance by enhancing the electron injection to give more radiative recombination

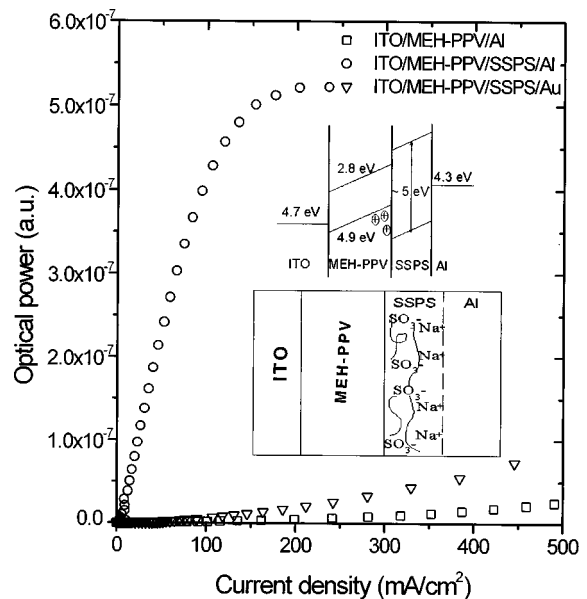


FIG. 4. Optical power vs current density characteristics for the devices with ionomers. The inset contains the scheme of the band alignments (top one) and the illustration of the bridging effect (bottom one).

with the oppositely charged carriers to form the excitons in MEH-PPV layer. Furthermore, the probability of radiative recombination should become higher due to the accumulation of holes at the MEH-PPV/SSPS interface, since the hole transport will be blocked by the energy barrier of SSPS ionomer leading to more balanced injection and efficient bipolar recombination. Since the SSPS ionomer has a very high bandgap (~ 5 eV) as obtained from the optical absorption spectrum, it may be very difficult for the hole to be injected into the ionomer as seen in the top inset in Fig. 4. This behavior is expected also in the two-layer structure device fabricated with the high work function Au cathode.

The role of the ionomer in enhancing the device performances exhibited in our system can now possibly be explained. As previously mentioned, part of the SSPS ionomer consists of ionic aggregations of sulfonic polyanions and sodium cations, where the permanent dipoles or the ionic groups are assumed to form some ordered arrangement in the aggregated regions. Under the electric field they may be disturbed and eventually broken or destroyed like the order-disorder transition. In our device of ITO/MEH-PPV/SSPS/Al the transition is observed at an electric field strength greater than 2.7×10^7 V/m, corresponding to 2 V. This is well confirmed by impedance spectroscopic analysis with dc bias voltages of 0, 1, 2, and 3 V as will be described in detail elsewhere.¹⁴ In brief, the impedance behaviors under the bias voltages of 0 and 1 V are quite different from those under 2 and 3 V. A very sharp increase of the impedance is observed in the frequency range of 3×10^4 – 1.5×10^6 Hz at above 2 V of bias. In general, this frequency region corresponds to the resonance frequency of the ions. It should be remembered here that the threshold voltage for the detection of light emission is about 2 V. According to our further investigation, the same behavior is also observed for the ITO/SSPS/Al device at above 2 V, but not for ITO/MEH-PPV/Al. Consequently, we can conclude that the unusual behavior originates from the SSPS layer. However, the ITO/SSPS/MEH-PPV/Al device does not show the sharp increase in impedance measurements. This is in contrast to the device based on the ITO/MEH-PPV/SSPS/Al system.

When the SSPS ionomer layer is placed next to the Al electrode, the sodium ions may independently arrange (or bridge) to the adjacent Al cathode by the applied electric field as seen in bottom inset in Fig. 4. Then electron injection might easily occur through the interaction between the metal ion and the cathode. This can happen only in a disordered state obtained under a certain electric field, because the ionic aggregates in the ordered state are neutralized themselves and their movement is restricted by highly crowded hydrocarbon molecules. This can be a reason why there is current flow and light emission in the case of ITO/MEH-PPV/SSPS/Au even though there is larger energy barrier between SSPS and Au. On the other hand, when the SSPS ionomer layer is placed next to the ITO, the sulfonic polyanions will hardly arrange to the adjacent ITO, because the polyanions are bound to the hydrocarbon pendant group by primary bonding and the hydrocarbon molecules are too bulky and heavy to move even at high electric fields. Although the origin of this interesting effect has yet to be established, it is intriguing to speculate that more efficient light emission is

related to excellent electron injection at the SSPS/Al interface due to the bridging effect through the arrangement of the sodium ions to the Al cathode.

As far as EL devices incorporated with ionic species are concerned, they can be now classified into three distinct types: the light-emitting electrochemical cell (LEC),¹⁵ the light-emitting diode based on self-assembled heterostructures,¹⁶ and the polymer light-emitting diode with ionomer shown in this work. In spite of their different roles in the emitting mechanism, it should be noticed that all the ionic materials used to fabricate light emitting diodes dramatically improve the device performances. The ionomers used in this work may offer better opportunities for improvement of polymer light-emitting diodes, if the polyanions, the matrix polymer, and the metal ions in ionomers are designed properly and optimized. This fact is based on the possibility that the various ionomers with desired structure can be artificially prepared. Further optimization of both the ionomer and the device structures is in progress.

In summary, we have investigated the polymer LED with SSPS ionomer used as an electron injecting and hole blocking layer. It is found that the performance of the ITO/MEH-PPV/SSPS/Al device is significantly enhanced due to the excellent electron injection and the hole blocking by the ionomer. The operating voltage is reduced by $\sim 60\%$ and the relative quantum efficiency is enhanced by a thousandfold compared with the corresponding single-layer MEH-PPV device. We attribute the efficient electron injection to the bridging effect between the Al cathode and sodium ions at the SSPS/Al interface.

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