Enhanced electron injection in polymer light-emitting diodes: polyhedral oligomeric silsesquioxanes as dilute additives

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Abstract

By blending monochlorocyclohexyl- polyhedral oligomeric silsesquioxanes (MCC-POSS) into poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1.4-phenylenevinylene (MEH-PPV), enhanced luminous efficiency (LE, cd A^{-1}) and brightness were observed in polymer light-emitting diodes (PLEDs) using Al as the cathode. PLEDs made from MEH-PPV with 0.5 wt.% of MCC-POSS exhibit LE of 1 cd A^{-1}, four times higher than that observed in simple MEH-PPV devices. x-ray diffraction studies, measurements of photovoltaic response and measurements of photoconductivity from the films of pure MEH-PPV and MEH-PPV with MCC-POSS demonstrated that the improved device performance results from mixing of MCC-POSS with MEH-PPV. The enhanced electron-injection into the emissive layer results from the effect of the ionic conductivity introduced by the addition of MCC-POSS.

Introduction

An ongoing research emphasis for polymer light-emitting diodes (PLEDs) reflects the need to tune the polymer–electrode interface to approach a balanced charge carrier injection for achieving high efficiency. A second area of ongoing importance is the need to improve the thermal stability of PLEDs.

Typically low-work-function metals (Ca and/or Ba) and alkali earth metal oxides (CaO and/or BaO) are necessary for obtaining adequate high efficiencies in PLEDs [1,2]. However, devices fabricated with these materials must be hermetically sealed for achieving long storage life and long stress life [3]. Thus, the possibility of achieving high performance PLEDs with Al as the cathode material is particularly attractive. Earlier work demonstrated that the device luminous efficiency can be dramatically improved with Al as the cathode by balancing the charge carrier injection through blending electron-transporting materials, surfactants and soluble metal ionic polymers into the emissive polymers [3–5]. Similar improvements were demonstrated by inserting alkali metal fluorides at the interface between the Al cathode and the emissive layer [6]

Many approaches have been used in attempts to improve the stability of conjugated polymers [7–9] In an earlier study, [10] we demonstrated that semiconducting polymers, poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1.4-phenylenevinylene (MEH-PPV) and poly(9,9-dioctylfluorene) (PFO), with improved thermal stability, with reduced chain mobility and with a decrease in the electroluminescent spectral features associated with excimer formation can be achieved by chemically incorporating polyhedral oligomeric silsesquioxanes (POSS) into the conjugated polymer chain (end capping with POSS). We also found that higher external quantum efficiency and luminance were achieved from PLEDs made from semiconducting polymers with POSS as an end capping moiety. However, a major hurdle in the use of such silsesquioxanes in PLEDs has been the relatively complex synthesis [11].

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R= cyclohexyl
MCC-POSS

MEH-PPV

Where   R =
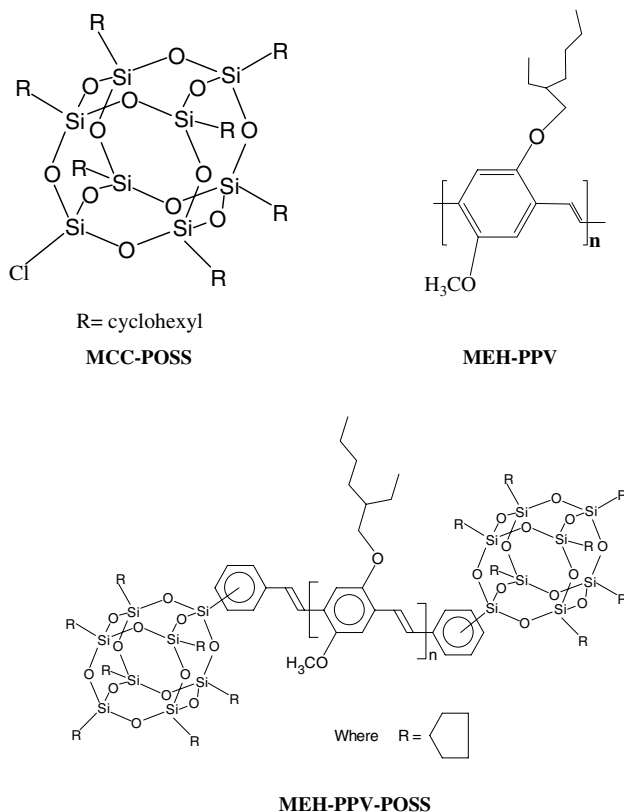
MEH-PPV-POSS

Scheme 1. Molecular structures of MEH-PPV, MEH-PPV-POSS and MCC-POSS.

In this study, we report that device efficiencies for PLEDs fabricated with Al as cathode are increased when MEH-PPV is blended with monochlorocyclohexyl- polyhedral oligomeric silsesquioxanes (MCC-POSS). X-ray diffraction (XRD) indicated that MCC-POSS is mixed with MEH-PPV, thereby improving the film morphology resulting in improved device performance. In addition, comparative studies of photovoltaic devices and steady-state photoconductivity from MEH-PPV and MEH-PPV with different concentrations of MCC-POSS indicated that the improved device efficiencies resulted from enhanced electron-injection. We suggest that the enhanced electron-injection into the emissive layer results from the effect of the ionic conductivity introduced by the addition of MCC-POSS.

1. Experimental

The molecular structures of MEH-PPV, MCC-POSS and MEH-PPV-POSS are shown in scheme 1. The MEH-PPV and MEH-PPV-POSS were provided by Organic Vision (Canada). The synthesis of MEH-PPV-POSS was reported previously [10] The MCC-POSS was purchased from Hybrid Plastics.

For PLED fabrication, we employed only the single-active-layer configuration with poly(3,4-ethylene dioxythiophene): poly(styrene sulfonic acid) (PEDOT: PSS) on indium tin oxide (ITO) as the hole-injecting bilayer electrode. The device structure is (ITO)/PEDOT: PSS/MEH-PPV: MCC-POSS/Al or (ITO)/PEDOT: PSS/MEH-PPV-POSS/Al. Details of device fabrication and testing have been reported elsewhere [12,13]. We also used single-layer device configuration
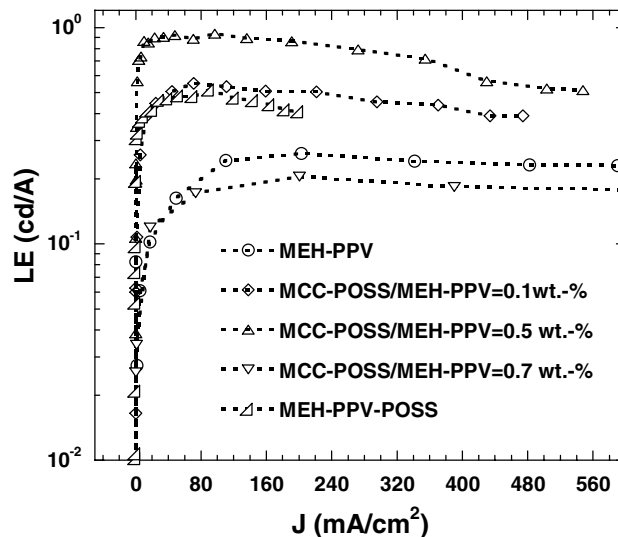

Figure 1. The luminous efficiency (LE, cd A^{-1}) as a function of current density (J, mA cm^{-2}) for the devices made from MEH-PPV with different doping concentrations of MCC-POSS, from pure MEH-PPV and from MEH-PPV-POSS.

to measure the open-circuit voltage for photovoltaic devices. The device structures are the same as used for PLEDs. The illumination intensity of white light is 35 mW cm^{-2}. The Al electrode was thermally deposited through shadow mask.

XRD was performed with CuK α radiation operating at 50 kV and 40 mA for wide- and small-angle measurements [14] The diffraction data were processed on an IBM workstation with interactive data language (IDL).

Steady-state photoconductivity was measured using the conventional modulation technique, whereby the light of an Xe lamp was dispersed by a monochromator and modulated by a mechanical chopper, while the photocurrent was measured by a lock-in amplifier [15,16] The samples were prepared in a surface configuration, with a gap ($\sim$200 μm) between the two Au electrodes. All measurements were performed in vacuum, at a pressure of about 10^{-4} Torr. The photocurrent spectra were normalized to constant illumination intensity.

2. Results and discussion

Figure 1 shows the luminous efficiency (LE, cd A^{-1}) as a function of current density (J, mA cm^{-2}) for the devices made from MEH-PPV with different doping concentrations of MCC-POSS, from pure MEH-PPV and from MEH-PPV-POSS. Devices fabricated with Al as cathode and MEH-PPV-POSS as the emissive layer exhibit significant improvement in LE over those fabricated using the same electrodes with MEH-PPV as an emissive layer. This is in agreement with our previous observations for PLEDs made by MEH-PPV and MEH-PPV-POSS using Ba/Al as a cathode [10] The principal differences in PLEDs made from pure MEH-PPV and MEH-PPV blended with MCC-POSS are the following.

1 The LE from PLEDs made from MEH-PPV blended with MCC-POSS is a few times larger than that from PLEDs made from pure MEH-PPV. For example, with 0.1 wt.% and 0.5 wt.% of MCC-POSS in MEH-PPV,
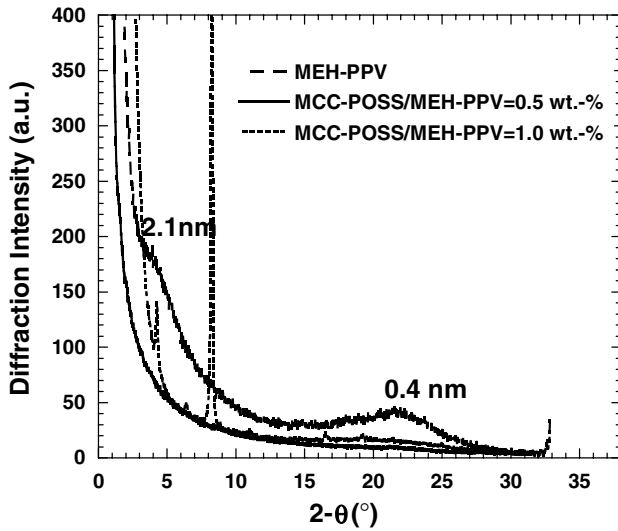
Figure 2. The intensity profiles of the diffraction patterns for pure MEH-PPV, MEH-PPV with 0.5 wt.% and 1 wt.% of MCC-POSS films spin-cast from toluene solutions.

Figure 3. The UV-Vis absorption spectra of the films made from pure MEH-PPV, MEH-PPV-POSS and MEH-PPV with different concentrations of MCC-POSS.

LE = 0.56 cd A^{-1} and LE=1 cd A^{-1}, respectively, i.e. larger than LE = 0.25 cd A^{-1} for pure MEH-PPV.

2 The devices made from MEH-PPV blended with MCC-POSS exhibit higher luminance (L, cd m^{-2}. For example, at J = 20 mA cm^{-2}, the L-values are 80 cd m^{-2}, 210 cd m^{-2} and 40 cd m^{-2} for 0.1 wt.%, 0.5 wt.% and 0.7 wt.% concentrations of MCC-POSS in MEH-PPV, respectively, whereas for the same J, the L of the pure MEH-PPV devices is 40 cd m^{-2}. Note that for MEH-PPV with 0.5 wt.% MCC-POSS devices, L is higher than in pure MEH-PPV devices. The brightness is over 2810 cd m^{-2} for the devices made from MEH-PPV with 0.5 wt.% MCC-POSS i.e. two times higher than that observed from identical devices made from pure MEH-PPV (1240 cd m^{-2}. However, at high concentrations of MCC-POSS, both L and LE decrease.

XRD was used to investigate the microstructure of the films made from pure MEH-PPV and MEH-PPV blended with different concentrations of MCC-POSS. Figure 2 shows the intensity profiles of the diffraction patterns obtained from films (spin-cast from toluene) of pure MEH-PPV, MEH-PPV with 0.5 wt.% and 1 wt.% of MCC-POSS, respectively. In the characteristic region of main chain stacking (2θ between $20°$–$27°$), all films show main chain stacking at $22.2°$, with a d spacing value of 0.4 nm. The films made from MEH-PPV with 1 wt.% of MCC-POSS also show intensity peaks at 2θ of $\sim$ 5 and $\sim 8.2°$. These peaks are from MCC-POSS crystal [17] indicating that there is some phase separation between MEH-PPV and MCC-POSS. The main difference in pure MEH-PPV and MEH-PPV with 0.5 wt.% of MCC-POSS films are the characteristic features at $2\theta = 22.2$ and $\sim 4.2°$. The MEH-PPV films show a characteristic peak at $\sim 4.2°$, with a d spacing value of 2.1 nm [18]. However, the MEH-PPV with 0.5 wt.% of MCC-POSS films do not show any peak in this region, indicating that the local structure of MEH-PPV is modified by blending with MCC-POSS. Moreover, the intensity of the peak at $22.2°$ observed for pure MEH-PPV is much stronger
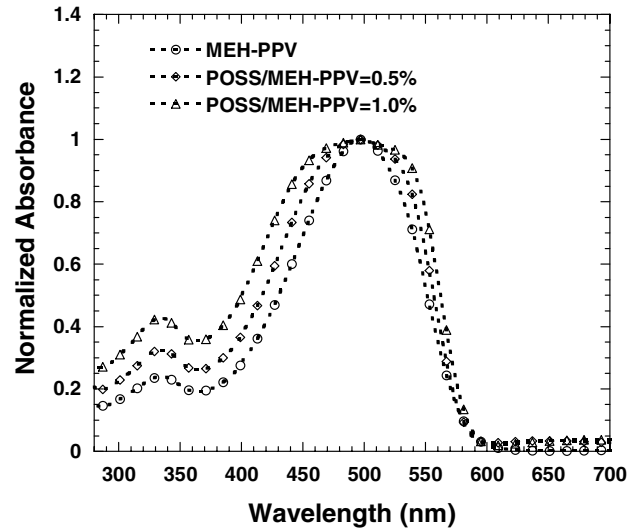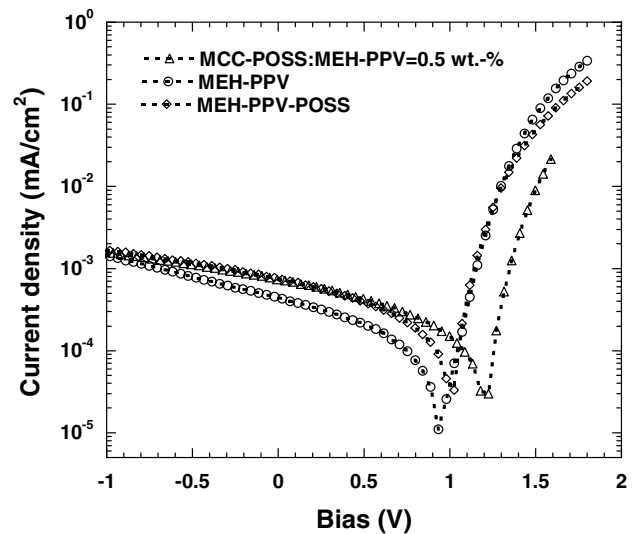

Figure 4. The comparisons of open circuit voltage from the devices measured with white light illumination. The devices' configuration is (ITO)/ PEDOT: PSS/polymers/Al devices. The polymers refer to pure MEH-PPV, MEH-PPV-POSS and MEH-PPV with 0.5 wt.% of MCC-POSS.

than that from MEH-PPV with MCC-POSS, implying that the pure MEH-PPV films have a better structural order. These results indicate that the MCC-POSS is mixed with the MEH-PPV structure.

The blue-shifted absorption spectra observed from MEH-PPV with MCC-POSS films is an additional evidence that MCC-POSS is mixed with the MEH-PPV. Figure 3 shows the UV–Vis absorption spectra of the films made from pure MEH-PPV and MEH-PPV with different concentrations of MCC-POSS. The blue-shifted absorption spectra indicated that the main chain of MEH-PPV becomes more disordered after blending with MCC-POSS. This is in good agreement with the comparisons of the data from oriented and non-oriented MEH-PPV and PPV films [19].
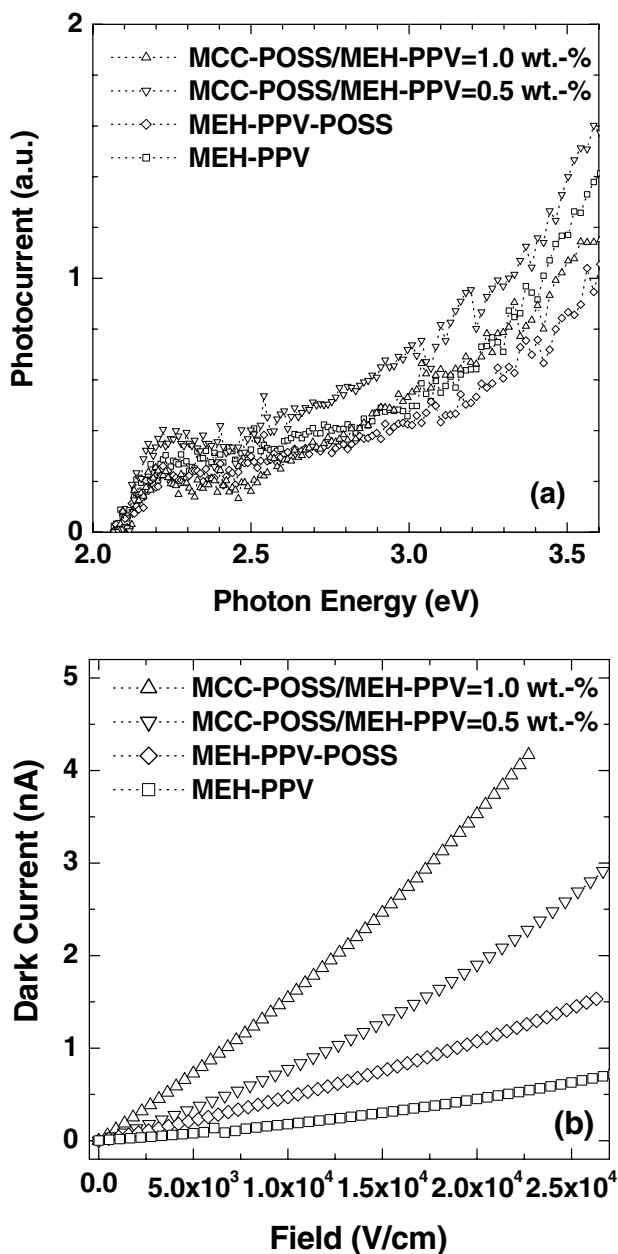
Figure 5. (*a*) The excitation profile of the steady-state photocurrents from polymer films and (*b*) the dark currents observed from these polymer films. Polymer films are pure MEH-PPV, pure MEH-PPV-POSS and MEH-PPV with 0.5 wt.% and 1.0 wt.% of MCC-POSS, respectively.

Compared with the devices made from pure MEH-PPV, the devices made from MEH-PPV with 0.5 wt.% of MCC-POSS have higher J and L implying better injection and/or transport. This might be due (at least in part) to a pinhole-free film on bilayer electrodes (ITO/PEDOT) and/or the improved adhesion to the ITO/PEDOT substrate, [20] an important requirement for electronic devices. Bao *et al* [21] reported that silsesquioxane resins formed pinhole-free thin films, much better, for example, than poly(3-hexylthiophene) cast from chloroform solution.

For insight into the origin of the improvements in device performance with an Al cathode in presence of the

MCC-POSS, photovoltaic measurements were carried out to determine the open circuit voltage. Current density–voltage curves were measured with the devices illuminated by white light. Figure 4 compares the open circuit voltage of (ITO)/PEDOT: PSS/polymers/Al devices (polymers: pure MEH-PPV, MEH-PPV-POSS and MEH-PPV with 0.5 wt.% of MCC-POSS). In the presence of MCC-POSS, the open circuit voltage increases from approximately 0.9 V (which is equal to the difference between the work functions of PEDOT: PSS and Al in the flat-band configuration) to about 1.25 V. Additionally, the open circuit voltage of the devices made from MEH-PPV-POSS is about 1 V. These demonstrated that the mobile ions within MCC-POSS alter the open circuit voltage. The increased open circuit voltages indicated that the MCC-POSS significantly enhances the built-in potential in the metal–semiconductor–metal diodes. Thus, the mobile ions within MCC-POSS lower the effective barrier height for electron injection, leading to more balanced injection of electrons and holes. As a result, L and LE from MEH-PPV blended with 0.5 wt.% of MCC-POSS increase.

To further clarify the effects of MCC-POSS, photoconductivity (PC) measurements were carried out on films of MEH-PPV, MEH-PPV-POSS and MEH-PPV with 0.5 wt.% and 1.0 wt.% of MCC-POSS, respectively. Figure 5a displays the excitation profiles of the steady-state photocurrent obtained from these films. The data observed from pristine MEH-PPV indicate a rise of the photocurrent coincident with the optical absorption and a weak dependence of the photocurrent waveform on photon energy, as previously reported. [15] The apparent rise of the PC at the highest energies is the result of a spurious contribution from electron photoemission [15]. All the films obtained by blending MEH-PPV with MCC-POSS at the concentrations we investigated show, within the experimental error, the same photocurrent waveform and photocurrent intensity as that of pristine MEH-PPV, indicating that the introduction of POSS or MCC-POSS in MEH-PPV either by chemical bond or by physical blending probably does not alter the quantum efficiency for charge carrier photogeneration, the carrier mobility or the carrier lifetime. We note that although there is structural similarity between MCC-POSS and C_{60}, their electronic properties are very different. C_{60} is known to considerably enhance the PC of MEH-PPV via photoinduced charge transfer. [16] However, our PC measurements clearly show that MCC-POSS does not behave like an electron acceptor in MEH-PPV. Figure 5b displays the dark currents observed from the films of MEH-PPV, MEH-PPV-POSS and MEH-PPV with 0.5 wt. % and 1.0 wt.% of MCC-POSS. The enhanced dark conductivity in MEH-PPV (proportional to the concentration of MCC-POSS) and the enhanced dark conductivity in MEH-PPV-POSS are likely due to the introduction of mobile ions from MEH-PPV-POSS and MCC-POSS.

Since ionic conductivity in an electroluminescent polymer can lead to *in situ* electrochemical doping and the formation of a p–i–n junction, as in light-emitting electrochemical cell, [22, 23] the mobile ions from MCC-POSS would be expected to improve the injection at the electrodes and thereby result in an improvement of the device performance.

3. Conclusion

In summary, we have demonstrated that improved luminous efficiencies can be achieved for PLEDs with Al as the cathode by blending the emissive conjugated polymer with polyhedral monochlorocyclohexyl- polyhedral oligomeric silsesquioxanes (MCC-POSS). XRD studies indicated that MCC-POSS are mixed with MEH-PPV, thereby affecting the morphology of MEH-PPV films and resulting in improved device performance. Additionally, the investigation of photovoltaic devices and steady-state photoconductivity from MEH-PPV and MEH-PPV with different concentrations of MCC-POSS demonstrated that the improvement in the device efficiency results from enhanced electron-injection associated with the ionic conductivity of MCC-POSS in the emissive layer.

Acknowledgment

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