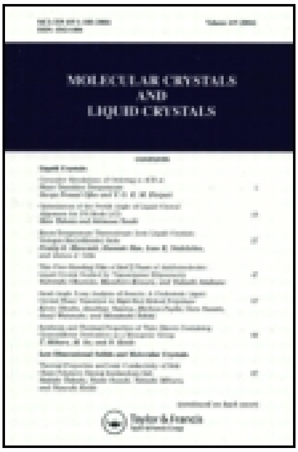

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photosensitivity of MEH-PPV Sandwich Devices and Its Implication to Polymer Electronic Structure

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Version of record first published: 04 Oct 2006.

To cite this article: G. Yu , K. Pakbaz , C. Zhang & A. J. Heeger (1994): Photosensitivity of MEH-PPV Sandwich Devices and Its Implication to Polymer Electronic Structure, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 543-548

To link to this article: http://dx.doi.org/10.1080/10587259408039289

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 543–548
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PHOTOSENSITIVITY OF MEH-PPV SANDWICH DEVICES AND ITS IMPLICATION TO POLYMER ELECTRONIC STRUCTURE

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Abstract Thin film devices made with Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene), MEH-PPV, are known to be efficient light emitting diodes. The same devices, under reverse bias, exhibit excellent photosensitivity. Large photovoltages were observed in devices with selected metals as the cathode and anode electrodes. The open-circuit voltage, V_{oc}, varies with the work functions of the electrodes; in most cases, V_{oc} approaches the work function difference between the two electrodes at high excitation levels. The photosensitivity increases significantly under reverse bias. At -10 V, the sensitivity in Ca/MEH-PPV devices reaches 45 mA/Watt at 20 mW/cm^2 (quantum yield of ~13% electrons/photon). The action spectra of the photovoltaic signal at zero bias, and the photocurrent at 2V forward bias follow the absorption spectrum at the band edge. Thus, mobile carriers can be generated either by charge injection at the contacts or by interband photoexcitation, as observed in inorganic semiconductors.

INTRODUCTION

Light emitting diodes (LEDs) fabricated with conjugated polymers[1,2] have attracted broad attention due to their potential for use in display technology. One of the promising materials for use in polymer LED is MEH-PPV, a semiconducting polymer with energy gap of ~2.1 eV. MEH-PPV film emits red-orange light after charge injection or under light illumination.[2,3] An external quantum efficiency of ~1% photons/electron (ph/el) has been demonstrated for light emission from Ca/MEH-PPV/ITO layered devices.

On the other hand, photovoltaic effect has also been observed in devices fabricated from conjugated polymers with degenerate or nondegenerate ground states (such as polyacetylene and polythiophene).[4] This photovoltaic effect is understood to be due to mobile carrier generation by interband photoexcitation. However, nonradiative channels dominate the carrier recombination processes in most polymers in which photovoltaic effect has been observed.[4]

Recently, we found that the Ca/MEH-PPV/ITO devices, under reverse bias, exhibit excellent photosensitivity as photodiodes. Thus, they are dual-function devices of both light-emission and photo-detection.[5] In this paper, we study generally the photosensitivity of metal/MEHPPV/metal sandwich devices. Metals with different work function were selected as cathode and anode. We found that the V_{oc} varies with the work functions of the electrodes, in most cases, V_{oc} approaches the work function difference between the cathode and anode. For the Ca/MEH-PPV/ITO devices, the V_{oc} is ~1.6 V and the short-circuit current, I_{sc}, is ~6 μA/cm^2 under 430nm illumination of 20mW/cm^2. The sensitivity increases significantly under reverse bias. At -10 V, the sensitivity is 45 mA/Watt at 20mW/cm^2. The action spectra of the photovoltaic signal at zero bias, and the photoconductive response at 2V forward bias follow the absorption spectrum at the band edge, indicating that mobile carriers can be generated either by charge injection at the contacts or by interband photoexcitation.

EXPERIMENTAL

The device used in this study consists of a metal (Ca, Al or In) contact on a MEH-PPV film cast on a glass substrate, partially coated with a layer of indium-tin-oxide (ITO) or a layer of semi-transparent gold, i.e., a sandwich configuration similar to that reported in electroluminescence (EL) experiments.[2] The size of each device is 0.1 cm^2.Details on the polymer synthesis and device fabrication can be found in literature.[5,6]

The current-voltage (I-V) characteristics were measured with a Keithley 236 Source-Measure Unit. The excitation source was obtained from a tungsten-halogen lamp filtered with a bandpass glass filter (λ_0=430nm, $\Delta\lambda$=100nm) and then collimated to form a homogeneous illumination area of ~0.5cmx1cm. The maximum optical power at the sample is 20 mW/cm^2 as measured by a calibrated Si photodiode. A set of neutral density filters were used for measurements of intensity (I_L) dependence. All the I-V experiments were performed with the devices in a dry box or in a vacuum chamber.

RESULTS AND DISCUSSIONS

Fig. 1 shows a typical I-V characteristic for a Ca/MEH-PPV/ITO device with polymer film thickness of ~800Å; forward bias is defined as positive voltage applied to the ITO contact. Transport under forward bias can be classified into three regions. A very small current (<10^{-9}A/cm^2) can be detected below 1.3 V; this is dominated by leakage through the device. In the range 1.3-1.8V, the current increases exponentially with voltage, by more than four orders of magnitude. This turn-on at ~1.3V is independent of the thickness of the polymer layer. The increase rate of the forward current diminishes for V>1.8V, carrier transport in this region is dominated by tunneling or space charge limited transport.[2,7,8] In reverse bias, the current saturates at ~10^{-11} A/cm^2 for voltages less than 2.5 V. At V_0~-2.5V, the current begins to increase superlinearly. This "turn-on" voltage in reverse bias scales with the polymer film thickness; i.e. the reverse bias current turns-on at field strength of E_0~$3x10^5$ V/cm. The rectification ratio (R_r) of this device is plotted in the inset of Fig. 1; $R_r > 10^6$, comparable to the best known polymer devices. EL becomes detectable in Ca/MEH-PPV/ITO devices in forward bias for V>2.0 V, and visible under room light for currents larger than 1 mA/cm^2. The emitted light is proportional to the current with external quantum efficiency of ~1% ph/el for V>2.5 V, similar to that reported earlier.[2] The EL efficiencies in devices with In or Al cathodes are significantly lower than that of Ca devices due to the inefficiency of electron injection at the cathode interface.[7,8]

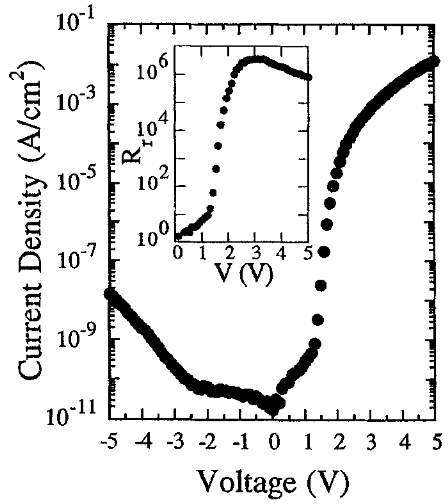

Fig. 1 Dark I-V characteristics of a Ca/MEH-PPV/ITO device. The rectification ratio Rr is shown in the inset.

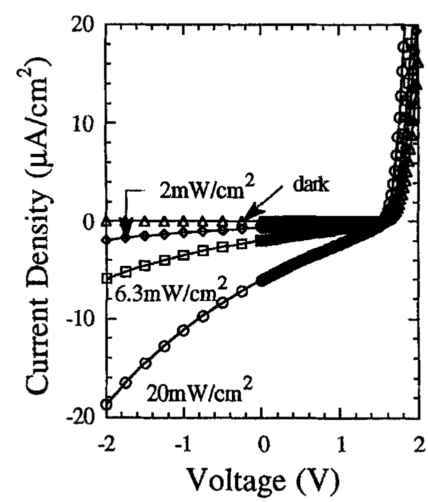

Fig. 2 I-V dependence in the dark and under 430nm illumination.

Assuming an electronic structure similar to inorganic semiconductors, a photovoltaic effect is expected for the MEH-PPV device . This, indeed, is observed as shown in Fig. 2, where the I-V dependences in a Ca/MEH-PPV/ITO device are plotted for the device in the dark and under illumination of 2, 6.3 and 20 mW/cm^2. At 20mW/cm^2, the V_{oc} saturates at ~1.6 V, and the I_{sc} is 6.1μA/cm^2. The energy conversion efficiency at low light levels is about 0.03%, similar to that observed in PPV devices.[9-11] The corresponding quantum yield at zero bias is ~0.2% (el/ph). As show in Fig. 2, the current under illumination crosses over the dark current at a voltage close to V_{oc}. This effect has been commonly seen in organic devices.[4] In contrast, in inorganic devices the current under illumination is commonly lower than the dark current at a given voltage.[12]

In Fig. 3, the V_{oc} and the I_{sc} are plotted as functions of illumination light intensity (I_L) for a Ca/MEH-PPV/ITO device with T≈800Å. The I_{sc} follows a power law dependence with I_L (i.e., I_L^{α}) over five orders of magnitude, with no signature of saturation under the highest I_L in the experiment (20 mW/cm^2). The exponent α is close to unity (i.e., a linear dependence) for device with T<1000Å, and reduces to 0.8 for device with T~1600Å. The V_{oc} has an approximately logarithmic relation with I_L for V_{oc} between 1.3 and 1.6 V (in which the dark current varies with voltage exponentially), it decreases faster for V_{oc}<1.2 V. At a given I_L, V_{oc} decreases slightly in devices with thicker polymer films. Similar effect was also observed in devices with other metal contacts. The V_{oc} varies with the cathode metal materials for devices with ITO anode, it decreases from 1.6 V to 1.1 V and 0.85 V for Ca, Al and In. However, the I_{sc} is less sensitive to the cathode material, remains ~5μA/cm^2 under 20mW/cm^2. For a given cathode, the V_{oc} increase by ~0.1-0.2 V by substitution of the ITO anode with Au. At high illumination level, the V_{oc}, in most cases, approaches the work-function (W) difference between the cathode and the anode. For example, for Ca/MEH-PPV/ITO devices, V_{oc}≈1.6V → W(ITO)-W(Ca), where W(ITO)=4.5-4.7eV and W(Ca)=2.9-3.1eV. Devices with Al cathode are exceptions; V_{oc}>W(ITO)-W(Al) where W(Al)≈4.4 eV. Band bending at the Al/polymer interface was suggested as the origin of the observed energy barrier.[9] Since V_{oc} of ~1.7V, ~1.8V and ~1.2V were also observed in Ca/PPV/ITO, Ca/BCHA-PPV/ITO and Al/PPV/ITO devices,[5,9,10] V_{oc} seems insensitive to the width of the energy gap of the semiconducting polymer used.

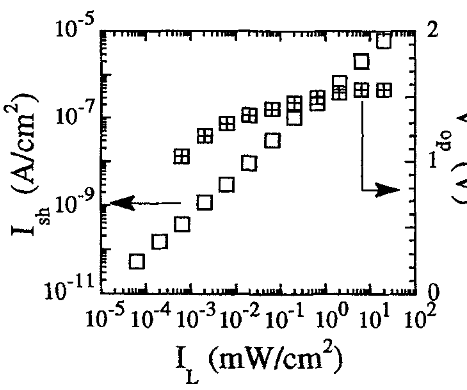

Fig.3 V_{oc} and I_{sc} of a Ca/MEH-PPV/ITO device as functions of I_L.

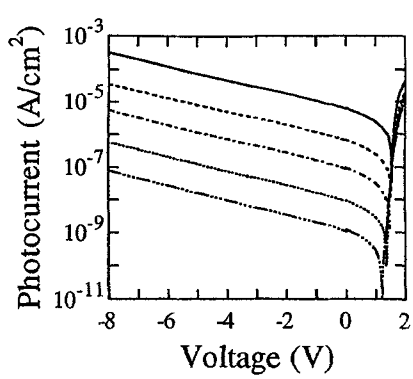

Fig. 4 Absolute photocurrent vs bias for several I_L (from top to bottom, 20, 2, 0.2, 0.02 mW/cm^2).

The photosensitivity increases significantly under reverse bias. In Fig. 4, the photocurrent, I_{ph}, from a Ca/MEH-PPV/ITO device is plotted as a function of bias voltage for several I_L. The I_{sc} increases exponentially with the reverse bias. At -8 V, I_{sc} reaches 0.33 mA/cm^2 under 20mW/cm^2. The corresponding photosensitivity and quantum yield are 16 mA/W and 4.8% ph/el. At -10V, these numbers increase to 45 mA/W and ~13% ph/el, respectively. Similar to I_{sc}, I_{ph} increases nearly linearly with I_L ($\sim I_L^{0.95}$) over the entire range measured. This is shown in Fig. 5a, in which the I_{sc} and

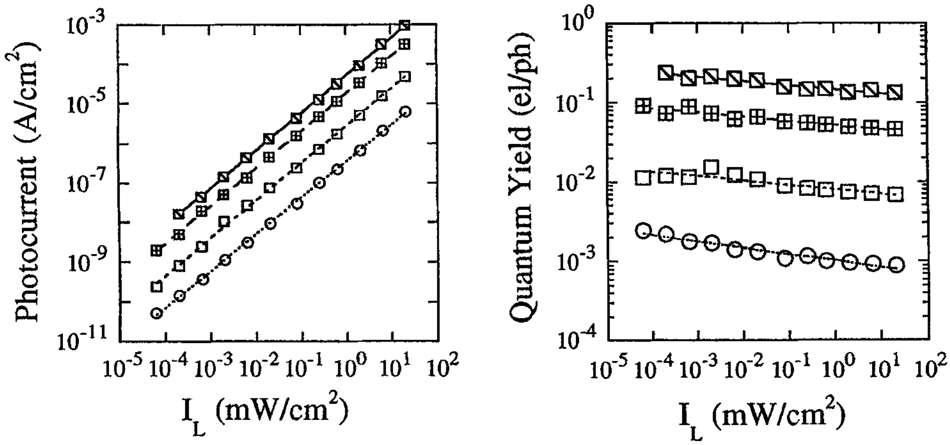

Fig. 5 Photocurrents (a) and Quantum yield (b) of a Ca/MEH-PPV/ITO device as functions of I_L (from top to bottom, -10V, -8V, -4V and 0V).

the I_{ph} (at -4V, -8V, and -10V) are plotted. The corresponding quantum yields are plotted in Fig. 5b. Due to the slight sublinearity of the I_L dependence, the quantum yields are even higher at low I_L. At -10V, the quantum yield is >20% (el/ph) at I_L~1 μW/cm^2, comparable to that of commercial devices made from inorganic semiconductors). The rate of the exponential increase scales reciprocally with the polymer thickness; i.e., determined by the applied electric field (E_0~2.5x10^5 V/cm). The enhancement of the photosensitivity at reverse bias was generally observed for devices with different metal contacts. The rate of the exponential increase is insensitive to the metal electrodes used.

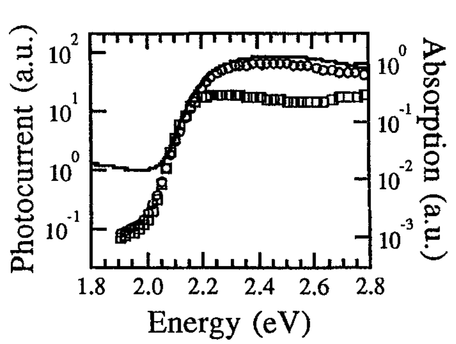

Fig. 6 $I_{sc}(h\nu)$ and $I_{ph}(h\nu)$ at +2V are compared with the absorption near the bandedge; (O) V=+2V, (□) V=0V and (—) absorption.

In Fig. 6, the spectral response of the I_{sc} and the I_{ph} at +2V are compared with the absorption spectrum. Both the $I_{sc}(h\nu)$ and the $I_{ph}(h\nu)$ at +2V follow the absorption spectrum near the band edge. Similar effect was also observed in I_{ph} from surface photoconductive cells.[13] This fact, along with the linear intensity dependence and the large photosensitivity, suggests mobile carrier generation by interband transition at E_g≈2.1 eV. If there were a significant exciton binding energy, the onset of the photovoltaic and the photoconductive responses would be blue-shifted with respect to the absorption.

In summary, we have characterized the photosensitivity and the photoresponse of metal/MEH-PPV/metal sandwich devices. These devices are not only efficient light emitting diodes, but also good photosensors; i.e., they are dual-function devices. The V_{oc} varies with the work functions of the metals used for cathode and anode, in most cases, approaches the difference of the work functions of the two electrodes. Photosensitivity increases significantly at reverse bias, to 45mA/Watt at I_L=20mW/cm^2. Both the I_{sc} and the I_{ph} follow the I_L linearly over five orders of magnitude, with no signature of saturation under the highest light intensity in the experiment (20 mW/cm^2). The action spectra of the photovoltaic signal and the photocurrent at forward bias follow the absorption spectrum at the band edge. These results suggest that mobile carriers can be generated either by charge injection at the contacts or by interband photoexcitation, similar to those observed in inorganic semiconductors. The excellent photosensitivity of polymer devices opens a way to the development of new types of low cost, large size and flexible polymer devices with potential for use in a wide range of applications.[14,15]

This work was supported by the Department of Energy under a grant from the Advanced Energy Projects, DOE93ER12138.

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