

## The Effects of H<sub>2</sub>O and O<sub>2</sub> on the Photocurrent Spectra of MEH-PPV

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### Abstract

Photocurrent (PC) and current-voltage measurements were taken on MEH-PPV [poly(2-methoxy-5-(2'-ethyl-hexyloxy)-para-phenylene vinylene)] in an as-made photocell, ITO / MEH-PPV (265 nm) / Al, in the photocell under ambient air, under a mixture of oxygen + nitrogen, and in vacuum after annealing. We discuss the different spectral responses and current-voltage characteristics obtained for the different atmospheres.

*Keywords:* Poly(phenylene vinylene) and derivatives, photoconductivity.

### 1. Introduction

The interaction of oxygen and water with conjugated polymers has recently attracted attention because their electronic properties change upon exposure to air [1-3]. For PPV, there is direct evidence that adsorbed water molecules modify the electronic properties of the surface [2]. We use measurements of photocurrent as a sensitive technique to separate the effects of water from those of oxygen on the whole of the polymer film.

### 2. Experimental Set-up

The device was illuminated through the ITO side, using a monochromated light from a tungsten lamp. A Keithley 237 Source-Measure-Unit was used to apply a dc bias voltage and to record the current. The spectra are corrected for the incident photon flux. The O<sub>2</sub> + N<sub>2</sub> atmosphere was obtained from a cylinder containing a mixture of 20% O<sub>2</sub> + 80% N<sub>2</sub>. The samples were first exposed to air, then annealed in vacuum and then exposed to oxygen, in each case for the time scales indicated in the figures.

### 3. Results and Discussion

Figure 1 shows PC action spectra for the device, in vacuum and in different exposures to oxygen. In the measured energy range [1.8 eV - 4.1 eV], the PC spectra can be divided into 4 different parts: **A** = Onset of first absorption band; **B** = First absorption band; **C** = Onset of second absorption band; **D** = Second absorption band + onset of third absorption band.

Upon exposure to oxygen and under forward bias, the PC is increased. This increase is stronger in B than in C. This suggests that oxygen mainly improves exciton dissociation at the ITO interface.

In contrast to this, the photocurrent in B is reduced for oxygen exposure under short circuit condition. In C, it is first reduced, then enhanced. We take the decrease in B to indicate increased trapping or decreased mobility of electrons due to O<sub>2</sub>. The current-voltage characteristics show a slightly higher dark conductivity with increasing oxygen exposure. Under illumination, the open-circuit voltage decreases with oxygen exposure. Thus, oxygen seems to affect the electrodes.

When the device is exposed to ambient air, that is to oxygen and water, we obtain a different spectral response (Figure 2). For forward bias, the photocurrent is now strongly enhanced at the onset of absorption and in C, but it is not as strongly enhanced in B. Thus, the photocurrent generation increases more next to the Al interface than in the bulk. We also observe a strong increase in D. For short-circuit conditions, the photocurrent immediately shows the two distinct peaks at the onset of absorption and in C, but this does not change with subsequent exposure. We attribute this spectral response mostly to the effect of oxygen rather than water by comparison with figure 1b. We note that the effects of air disappear after annealing in vacuum. The reduction of open-circuit voltage in the I/V curve is less pronounced than for only oxygen exposure.

Our results complement the photoelectron spectroscopy (PS) findings of Xing et al.[2] which show that surface-adsorbed water forms a Van-der-Waals complex with PPV that modifies the  $\pi$ -band edge. Under these conditions, Xing et al. observe no

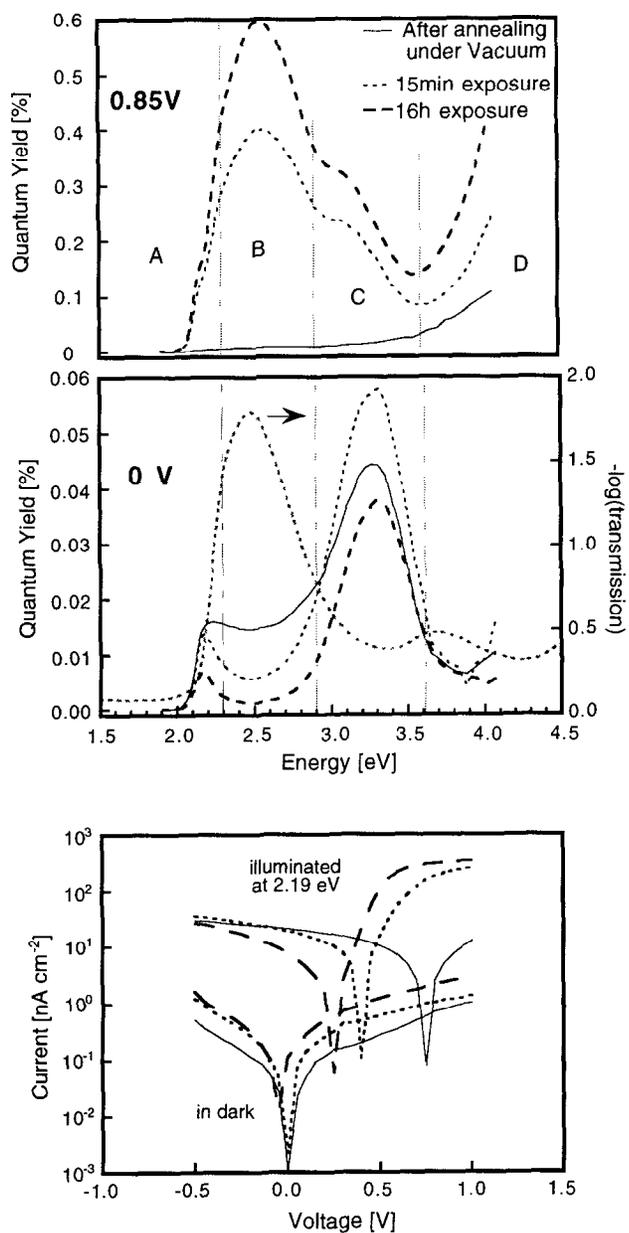


Fig. 1. PC action spectra under forward bias of 0.85V (top), under short-circuit condition (middle) and I/V characteristics (bottom) of MEH-PPV after exposure to  $O_2$ .

changes in the PS spectra upon exposure to oxygen, though it is well known that PPV can undergo photooxidation [4].

We do observe strong effects as described above due to oxygen, as our experiments were conducted in oxygen atmosphere (rather than in vacuum after oxygen exposure). We note that the increased exciton dissociation upon oxygen exposure occurs at the ITO interface, i.e. oxygen has to diffuse through the polymer film and the Al electrode to get there. Thus, we have shown that the bulk of the polymer is affected via diffusion. This is consistent with the increased trapping for reverse bias.

For exposure to water, we found the strongest effect at the

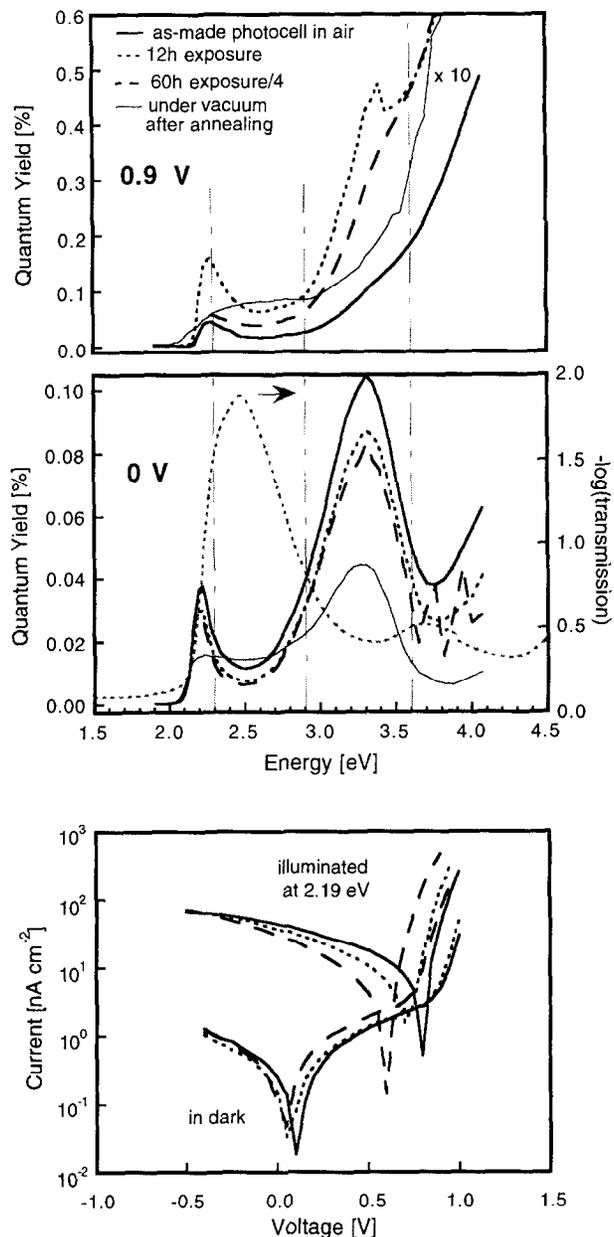


Fig. 2. Spectral Response of PC under forward bias of 0.9V (top), under short-circuit condition (middle) and I/V characteristics (bottom) of MEH-PPV in ambient air.

polymer / aluminium interface rather than in the bulk or at the polymer / ITO interface. Whether this is due to water adsorption at the MEH-PPV surface, that does not penetrate deeply into the film, or whether this is due to changes of the aluminium electrode, is currently under investigation. The fact that the photoconductivity is strongly reduced from the values in air after annealing is consistent with the findings of Xing *et al.* [2]

## 5. References

- [1] M.S.A. Abdou *et al.* J. Am. Chem. Soc. **119**, 4518 (1997).
- [2] K.Z. Xing *et al.* Adv. Mater. **8**, 971 (1996).
- [3] N. Chawdhury *et al.* Optical Mat. **9**, 498 (1998).
- [4] N.T. Harrison *et al.* Synth Met. **91**, 61 (1997).