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Electroabsorption studies of phthalocyanine/perylene solar cells

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Abstract

We report electroabsorption (EA) studies of electric fields in bilayer molecular organic solar cells made from zinc phthalocyanine (ZnPc) and a methyl substituted perylene pigment (MPP). We have detected an electric field at the metal/organic interface which is sensitive to the external DC bias. The interface field has a different spectral signature from that of the bulk of the two layers, which we attribute to interface species such as charge transfer-induced dipoles. The electric field is proportional to the applied bias in devices containing only ZnPc or MPP, but rectifying behavior is observed in the bilayer solar cell. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Electroabsorption; Semiconductor heterojunction; Molecular organic solar cell; Phthalocyanine; Perylene

1. Introduction

Organic semiconductors are promising materials for photovoltaic cells and other optoelectronic applications such as light emitting diodes (LEDs) and optical switches. Multilayer structures have been developed to optimise charge photogeneration and transport. Organic heterojunctions and metal/organic interfaces play an important role in device performance and elucidation of their electronic structure is therefore

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important to understanding and improving these devices. The most direct studies of such interfaces have been by ultraviolet photoemission spectroscopy (UPS) [1–3]. These studies have shown that the vacuum energy is shifted at the interface, but have not been able to directly determine the origin of this shift.

We present electroabsorption (EA) studies of organic solar cells made from zinc phthalocyanine (ZnPc) and a methyl substituated perylene pigment (MPP), N,N′-dimethyl-3,4:9,10-perylenbis (carboximid). We have also measured MPP and ZnPc single layer devices. A strong electric field develops at the organic heterojunction. The EA spectrum of the heterojunction field is different from that of the bulk of the two layers. This is direct experimental evidence for a shift of the vacuum level across the interface. The shift is attributed to a space charge region formed at the interface. Comparison of the EA spectra at different DC biases permits separation of the heterojunction and bulk EA spectra. We are then able to determine the dependence of the electric field in the single layer devices and bilayer solar cells upon the applied DC bias. The EA signal in single layer devices is proportional to the applied bias, but the solar cell exhibits rectifying behavior.

EA spectroscopy measures the effect of an electric field on the absorption of light. The EA spectrum is proportional to the square of the electric field and the imaginary part of the third-order DC Kerr nonlinear susceptibility [4]. Typically, an AC field is applied to the sample and lock-in amplification is employed. In the presence of a combined DC and AC electric field, the EA at the AC frequency $1f$ is proportional to $V_{AC} \times V_{DC}$ and the EA at twice the AC frequency $2f$ is proportional V_{AC}^2. This technique has been used to study electric fields in organic LEDs [5] and poling of multilayer polymer films [6].

Bilayer solar cells were produced by successive evaporation of MPP and ZnPc on glass substrates coated with indium tin oxide (ITO) obtained from Balzers, Liechtenstein. The dyes were evaporated in a convential HV evaporation system at rates of 0.4–0.6 nm/s for ZnPc and 0.5–0.8 nm/s for MPP under a vacuum below 4×10^{-6} mbar. A top electrode of gold was then evaporated onto the organic film. The photovoltaic characteristics of the solar cells are described elsewhere [7]. Single layer ITO/MPP/Au and ITO/ZnPc/Au devices were also prepared analogously.

For electroabsorption measurements, light from a xenon lamp was dispersed through a monochromator and focused onto the organic semiconductor device through the transparent ITO contact. The light reflected at the back metal electrode (and) was then focused onto a silicon photodiode. A combined DC and AC electric field was applied to the device. The AC test field modulated at 3.3 kHz was taken from the reference output of the lock-in amplifier and a programmable voltage source provided the DC bias. All measurements were performed in ambient air.

2. Experimental results and discussion

Fig. 1 shows the absorption spectra of ZnPc and MPP, measured with a Unicam spectrophotometer. ZnPc has a strong absorption band between 1.5 and 2.4 eV, with peaks at 1.75 and 2.02 eV. The absorption spectrum of MPP lies between 2 and 3 eV,

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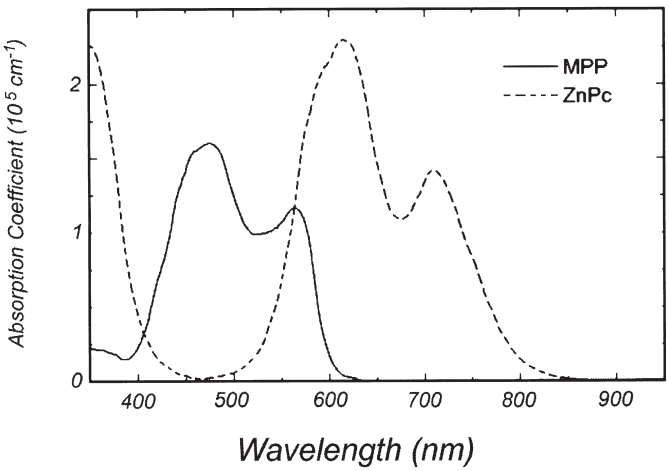

Fig. 1. The absorption spectra of ZnPc (dashed line) and MPP (solid line).

with peaks at 2.2 and 2.55 eV. Each material has strong absorption features where the absorption of the other material is weak or nonexistent. Therefore, the EA spectrum of the constituent layers of a solar cell will contain features that can be attributed to only one layer. The two materials are also well suited for bilayer solar cells as they provide good coverage of the solar spectrum.

Fig. 2 shows the electroabsorption spectra of ZnPc and MPP. An interdigitated array of metal electrodes was evaporated on top of the films. The measurements were conducted under 500 V AC bias across an electrode spacing of 10 μm at 300 K. Both spectra have an oscillatory lineshape with a number of clearly resolved features. The onset of the EA spectrum of ZnPc is at $\approx$ 1.4 eV and there are peaks at 1.49, 1.62, 1.76, 1.93, 2.07 and 2.17 eV. The onset of the EA spectrum of MPP is at $\approx$ 1.9 eV and there are peaks at 2.1, 2.17, 2.4, 2.52, 2.62 and 2.72 eV. As expected from their absorption spectra, the EA spectra can be clearly distinguished from one another and enable development of a complete model of the device.

Fig. 3 shows the 1*f* and 2*f* EA spectra of a single layer MPP device, measured with 2.5 V AC test bias. The 1*f* EA spectrum was measured with 1 V DC bias; the 2*f* EA spectrum was insensitive to the DC bias. The 2*f* EA spectrum has its onset at 1.9 eV, a peak at 2.05 eV and an oscillatory spectrum above this energy. The 1*f* EA spectrum also has a peak at 2.05 eV and the two spectra are normalized to this peak. However, the oscillatory portion of the 1*f* EA spectrum is opposite in sign to that of the 2*f* EA spectrum and subgap features are also observed. There should be no EA signal below the optical gap, though these features may be related to injected carriers. Further measurements need to be undertaken before we can make further comment on these differences. The spectral lineshapes were independent of the AC and DC biases.

The dependence of the 1*f* EA at 2.05 eV on the applied DC bias is shown in Fig. 4. The 1*f* EA is proportional to the DC bias and is nulled at -0.2 V, close to the value expected from the work function difference between ITO and gold (0.4 eV). The work

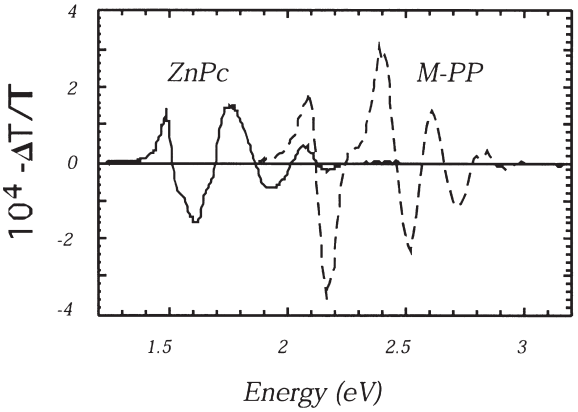

Fig. 2. The electroabsorption spectra of ZnPc (solid line) and MPP (dashed line).

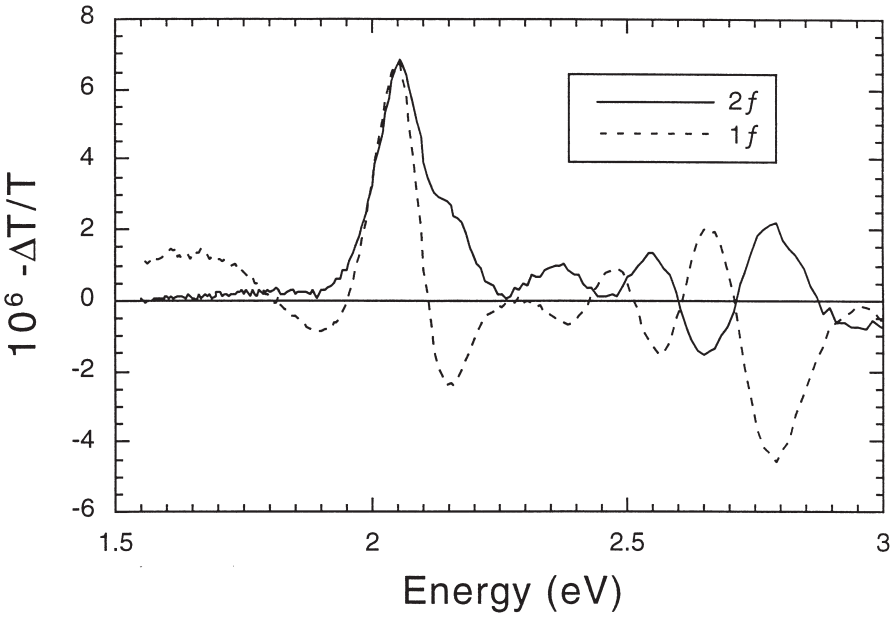

Fig. 3. The 1*f* and 2f EA spectra of an ITO/MPP/Au device.

function of ITO is quite sensitive to preparation conditions and so a small discrepency between the expected and measured values is not surprising. Previous measurements of an MPP device have shown an ohmic dependence on applied bias [8]. This is consistent with a linear dependence of the internal electric field on the applied bias.

Fig. 5 shows a series of 1*f* EA spectra of an ITO/ZnPc/Au device, measured with applied DC biases of -1.5, -1.0, -0.5, 0, 0.5 and 1.5 V . In contrast to the

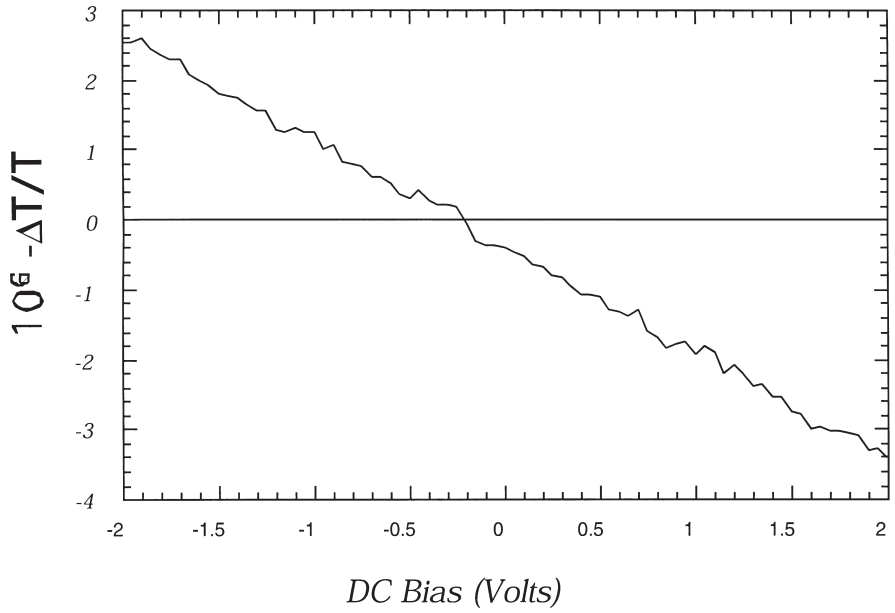

Fig. 4. The EA response of the MPP device vs. DC bias.

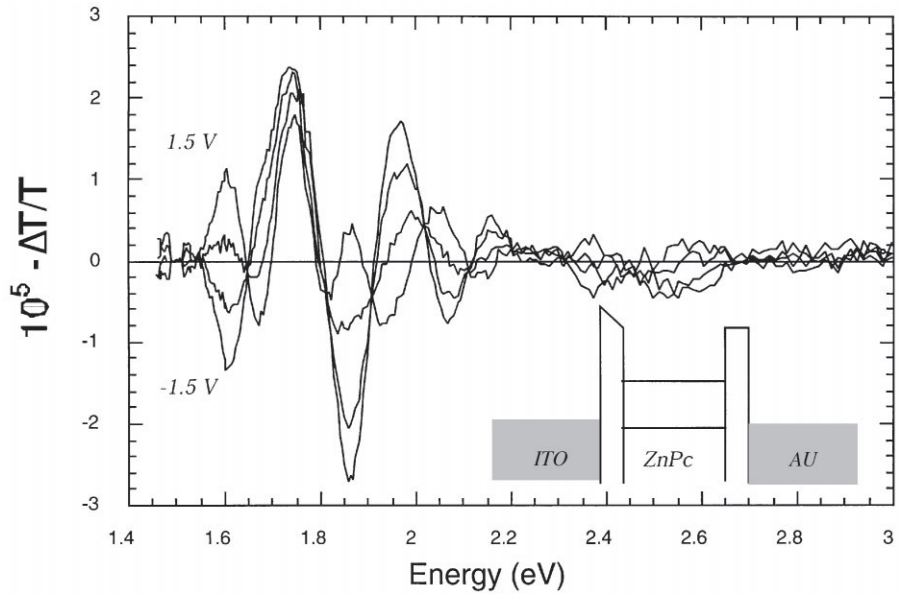

Fig. 5. EA spectra of an ITO/ZnPc/Au device at DC biases of − 1.5 V, − 0.5 V, 0.5 V and 1.5 V. The signal at 1.6 eV is negative for negative bias and positive for positive bias. Inset: A schematic diagram of the energy levels of the device.

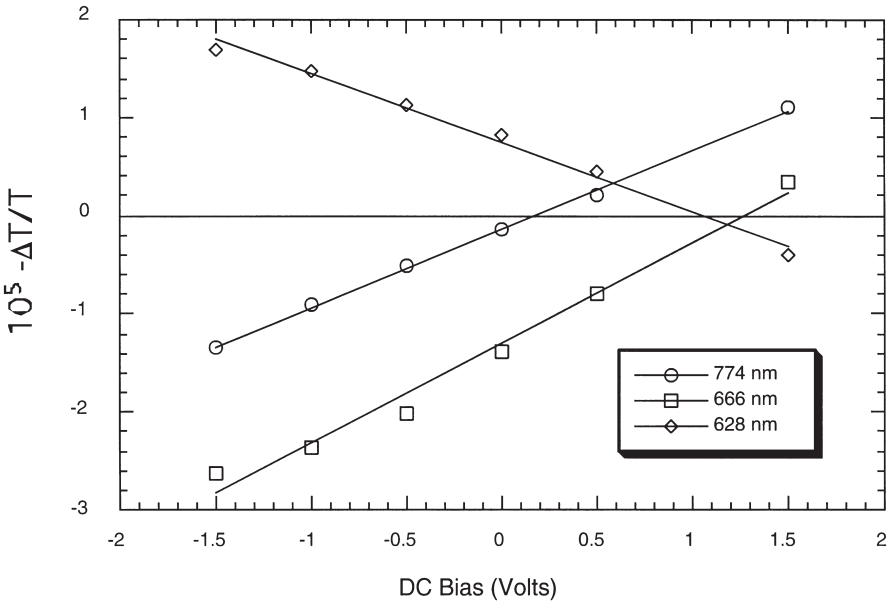

Fig. 6. The EA response of the ZnPc device vs. DC bias at 628, 666 and 774 nm.

measurements on MPP, the EA spectrum varies with the applied bias. Consider the EA peaks at 1.61, 1.73 and 1.86 eV. The 1.61 eV peak increases as the DC bias increases, changing from -1.3×10^{-5} at -1.5 V to 1.1×10^{-5} at 1.5 V. In contrast, the peak at 1.74 eV changes only from 2.4×10^{-5} at -1.5 V to 1.8×10^{-5} at 1.5 V. There are also shifts in the position of peak positions above 1.9 eV.

These shifts can be explained by considering the electronic structure of the ITO/ZnPc and ZnPc/Au interfaces. UPS studies of a number of metal/organic interfaces have shown that there is a shift in the vacuum energy level at the interface. It has been suggested that interface states such as charge transfer-induced dipoles shift the molecular energy levels of the organic with respect to the metal. Campbell et al. have demonstrated that a single monolayer is sufficient to shift the energy of an organic layer over a range of more than 1 eV [9]. Such interface states could have a different EA spectrum than that of the bulk. The 1*f* EA spectrum would then consist of two components: that of the interface, which is insensitive to the applied bias, and that of the bulk, which is proportional to the applied bias. It is also worth noting that ZnPc has different crystal structures. Differences in the local crystal field will mean a difference in the absorption and hence, the EA spectra. If one phase were preferentially formed near the electrode interface, this would also explain shifts in the EA spectrum.

Figs. 6 and 7 demonstrate the validity of this approach. Fig. 6 shows the 1*f* EA signal vs. DC bias, measured at three peaks of the EA spectrum. In all cases, there is a linear dependence on the DC bias. Thus, within the bulk of the ZnPc film, the internal electric field is proportional to the applied bias (accounting for work function

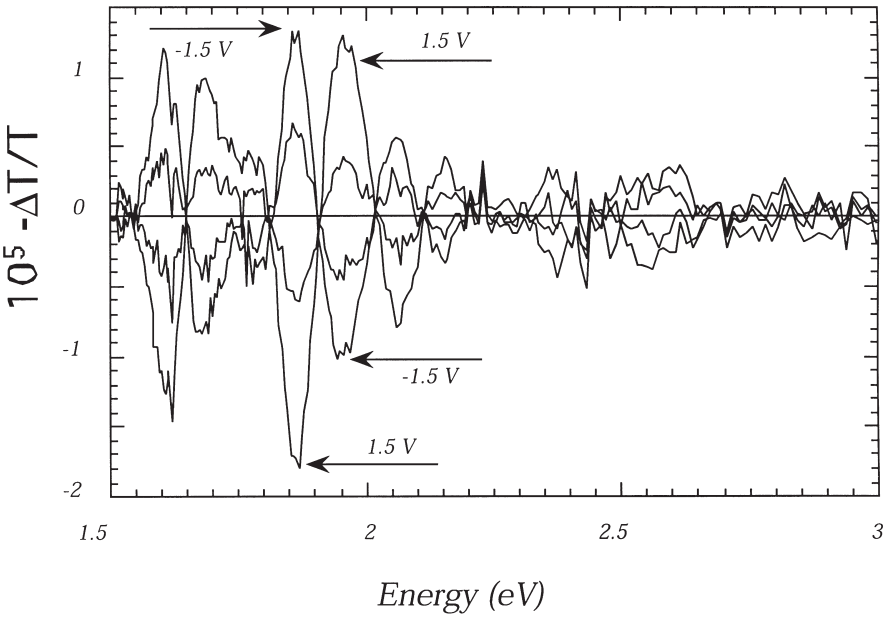

Fig. 7. The difference between the EA spectrum taken with no DC bias applied and that at − 1.5 V, − 0.5 V, 0.5 V and 1.5 V.

and interface effects). We can eliminate the contribution of the interface EA spectrum by taking the difference between any two 1*f* EA spectra. Fig. 7 shows the difference between the individual EA spectra and the spectrum measured with 0 V applied bias. Only the magnitude of the resulting difference depends upon the applied bias, not its lineshape. Hence the EA spectrum of the device consists of the sum of the contributions from one or both interfaces and the bulk. Fig. 8 shows the 2*f* EA spectrum which will be insensitive to any static electric fields, including that of the interface. This spectrum has the same lineshape as that of the difference of the 1*f* EA spectra, as would be expected.

Careful consideration of the 1*f* EA spectra permits deconvolution of the bulk and interface EA spectra. The 1*f* EA peak at 1.75 eV clearly originates from the interface. There are several points where all the individual EA spectra cross one another (1.65, 1.91 and 2.02 eV). These points would occur where there is a zero level crossing of the bulk EA spectrum and hence any EA signal must be entirely from the interface. From these considerations, the EA spectrum of the interface was determined and is shown as a dashed line in Fig. 8. Any of the 1*f* EA spectra can be simulated by a linear combination of the interface and bulk EA spectra. We thus clearly demonstrate that the vacuum level shift originates from an electric field at the interface which lies within the organic layer.

Fig. 9 shows a series of 1*f* EA spectra of an ITO/ZnPc/MPP/Au organic solar cell, measured at DC biases between − 0.5 and 0.5 V. Given that there is an ITO/ZnPc

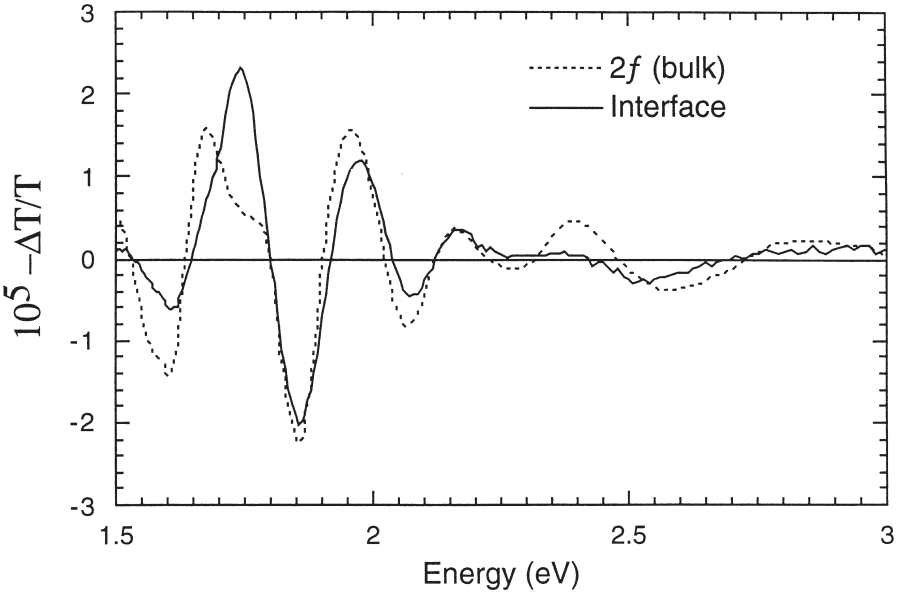

Fig. 8. The 2*f* (bulk) and interface EA spectra of the ZnPc device.

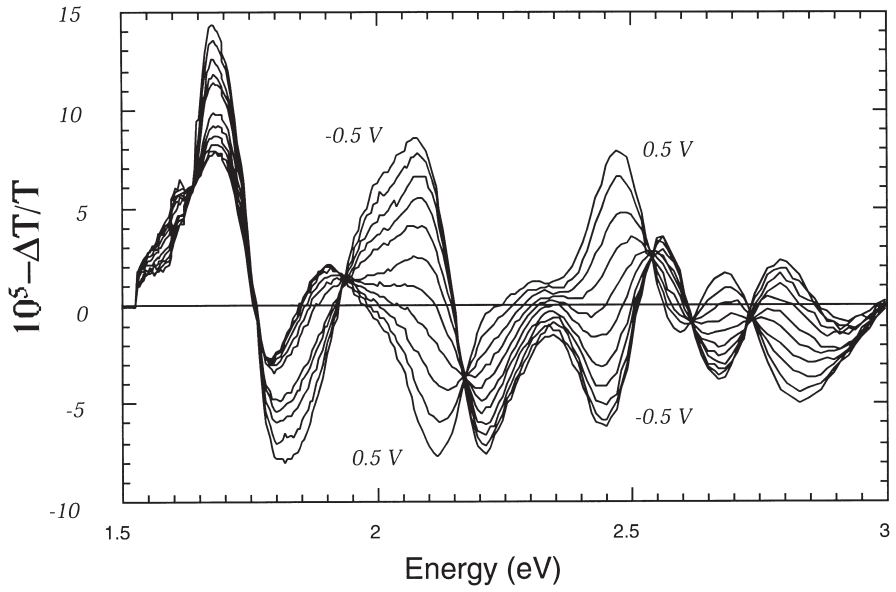

Fig. 9. The EA spectrum of the bilayer solar cell, measured with DC biases between − 0.5 V and 0.5 V in 0.1 V increments. The signal at 2.45 eV is negative for negative bias and positive for positive bias.

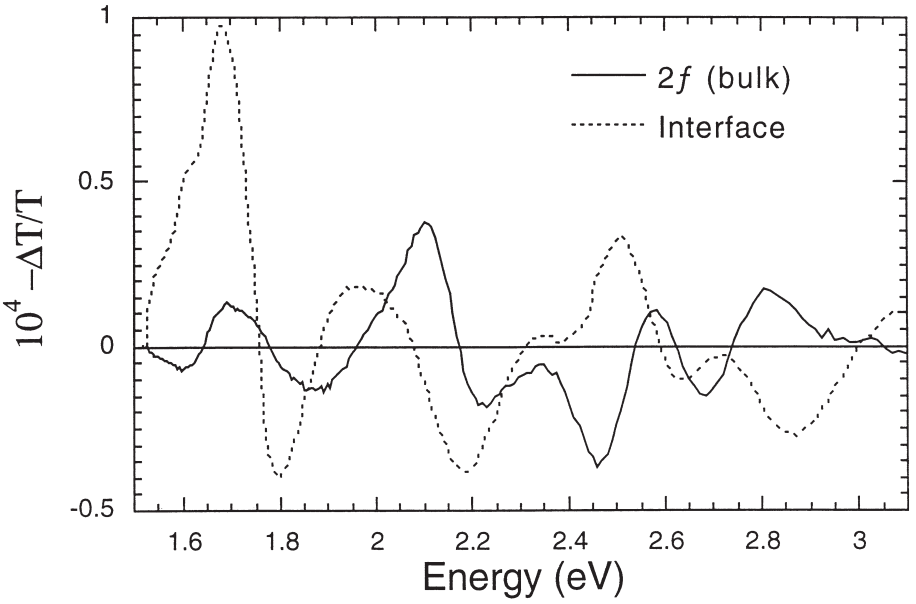

Fig. 10. The 2*f* (bulk) and interface EA spectra of the bilayer solar cell.

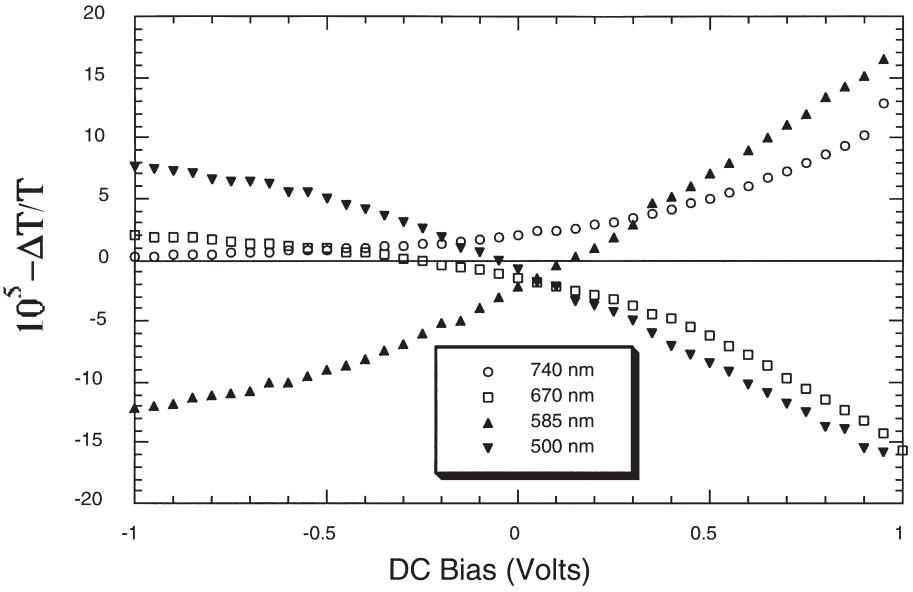

Fig. 11. The EA response of the bilayer solar cell vs. DC bias in the ZnPc layer (open symbols) and in the MPP layer (filled symbols).

interface, it is not surprising that the EA spectrum varies with the applied bias. The EA spectrum changes sign at some energies (2.1, 2.45, 2.8 eV), but not at others (1.7, 1.8, 2.2). All of the EA spectra have the same signal at 1.93, 2.17, 2.54, 2.62 and 2.74 eV. We proceed in the same manner as before to deconvolute the bulk EA spectrum from that of the interface(s). As before, we compare the $2f$ spectrum of the solar cell to the various $1f$ spectra in order to separate out the contributions from the interfaces (ITO/ZnPc and ZnPc/MPP) from that of the bulk of the layers. The $2f$ and the interface spectra are shown in Fig. 10. There are signficant differences between the interface EA measured on the ZnPc device and the solar cell. This suggests that an interfacial electric field also develops at the organic heterojunction.

Fig. 11 shows the bias dependence of the EA signal in the MPP layer (at 500 and 585 nm) and in the ZnPc layer (at 670 and 740 nm). Unlike for the MPP and ZnPc devices, the EA response of the solar cell exhibits rectifying behavior. This is significant evidence that a strong interfacial field cannot simply be the origin of the photovoltaic effect. If this were the case, we would expect to see a photocurrent from the ZnPC and bilayer device, but not the MPP device. Rather, the nature of the organic heterojunction determines the photovoltaic behavior of the device. This model is reported in more detail elsewhere in these proceedings [7].

3. Conclusions

We have shown that a strong electric field develops at both metal/organic interfaces and organic heterojunctions. The EA spectrum of the heterojunction field is different from that of the bulk of the two layers, due to a strong electric field at interfaces. Comparison of the EA spectra at different DC biases permits separation of the interface and bulk EA spectra. The EA signal in single layer devices is proportional to the applied bias, but the solar cell exhibits rectifying behavior. This is consistent with the development of a p/n junction at the ZnPc/MPP heterojunction.

Acknowledgements

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