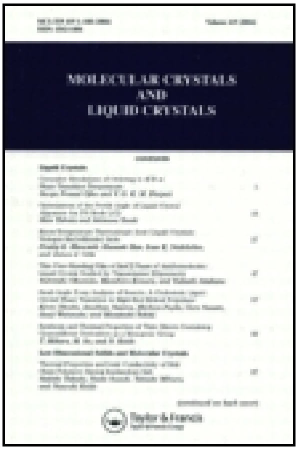

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COMPARISON OF ELECTROCHEMICAL AND SPECTROSCOPIC DATA OF THE LOW-BANDGAP POLYMER PTPTB

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To efficiently harvest the terrestrial solar emission in photovoltaic devices, the absorption spectrum of the photoactive material has to match the solar spectrum as well as possible. Materials which absorb at photon energies where the maximum of the solar emission occurs (around 1.8 eV are very important for photon harvesting.

The synthesis of Poly-(N-dodecyl-2,5-bis(2′-thienyl)pyrrole-(2,1,3-benzothiadiazole)) (PTPTB), a low bandgap polymer, and its use in 'bulk heterojunction' photovoltaic devices was recently reported. For better understanding of the properties of this material, spectroelectrochemical, optical spectroscopic and cyclovoltammetric measurements as well as electrochemical voltage spectroscopy (EVS) were carried out to determine both the electrochemical and the optical bandgap. The comparison of the results allows the prediction of charge carrier formation via light exposure.

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Keywords: low bandgap polymer; electrochemical voltage spectroscopy; energy diagram

1. INTRODUCTION

Conjugated polymers are an interesting class of materials for photovoltaic applications because of their easy processability and chemical tunability. The materials commonly used in the high efficiency organic solar cells [1,2] are MDMO-PPV [poly-(2-methoxyl, 5-(3,7 – dimethyloctyloxy)] para phenylene-vinylene): PCBM ([6,6]-phenyl C_{61} butyric acid methylester) blends. However, MDMO-PPV has a bandgap of 2.3 eV and thus can exploit only about 30% of the total photon flux under AM 1.5 [1,2]. Therefore emphasis is put on the research of conjugated organic materials with a bandgap around 1.8 eV or lower, to harvest a wider range of the solar spectrum.

Besides the width of the gap, which can be easily determined with absorption spectroscopy, also the energy levels of the valence band (VB) and the conduction band (CB) of the low-bandgap material have to fit into the energetics of a photovoltaic device. Electrochemistry is a powerful tool to determine the energetic positions [3–5] of the edges of VB and CB in terms of eV vs. vacuum level, since they correspond to the potential values for the onsets of oxidation and reduction in electrochemical reactions of conjugated polymers [6,7].

In this contribution, we show the possibility to generally predict photoinduced charge carrier formation and energetic suitability for electron transfer to a fullerene unit in a solar cell using electrochemical voltage spectroscopy (EVS) [3–5] as a method for determination of the onset values in combination with absorption spectroscopy and *in situ* spectroelectrochemistry. Furthermore, a comparison of the energetic levels of PTPTB and MDMO-PPV is presented.

2. EXPERIMENTAL

The synthesis of PTPTB was described previously [8]. Figure 1 shows the structure of PTPTB and MDMO-PPV.

All electrochemical measurements were carried out at room temperature in a glovebox under argon atmosphere. The supporting electrolyte was 0.1 M $(C_4H_9)_4N^+PF_6^-$ in acetonitrile. Cyclic voltammetry (CV) and EVS were carried out using a Jaissle potentiostat computer controlled with SCADA software. For both techniques the working electrode (WE) as well as the counter electrode (CE) were platinum foils. Polymer films were dropcast from toluene solutions onto the WE. As a reference electrode (RE) a silver wire coated with AgCl was used. After each measurement the RE was calibrated with ferrocene.

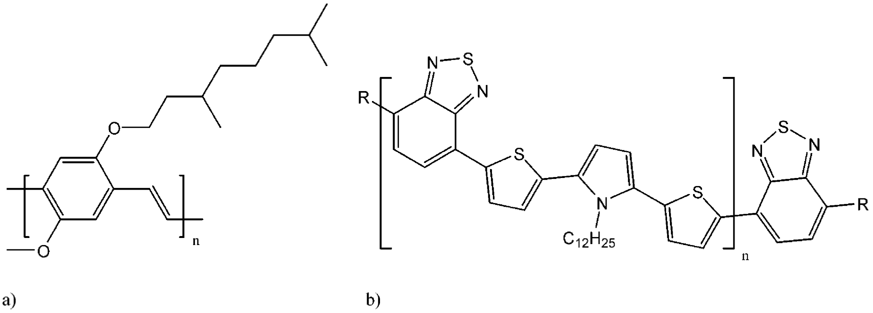

FIGURE 1 Chemical structures of a) MDMO-PPV and b) PTPTB; R = H, Br, n = 1–4.

The principle of EVS is shown in Figure 2. This method was developed to accurately measure charge/potential relationships under quasi-equilibrium conditions [5,6]. Initially the system is allowed to reach equilibrium at the starting potential *V*. Under computer control the potential is then stepped to a new value *V*+d*V* (Fig. 2a) and the subsequent flow of current is monitored and recorded, while the system reaches its new equilibrium

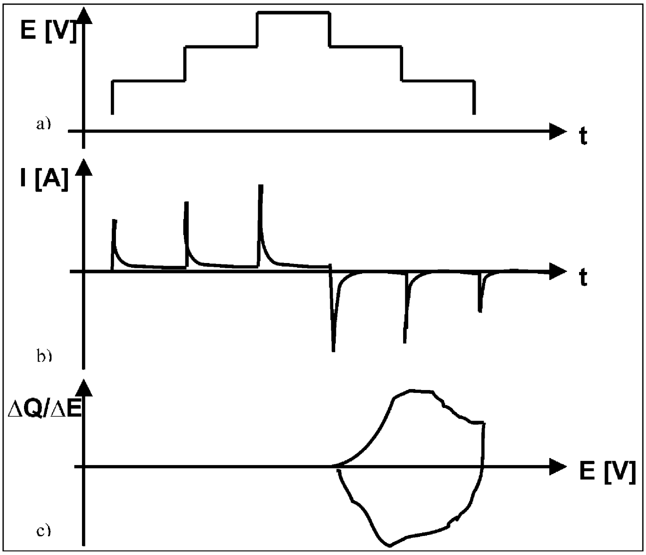

FIGURE 2 Principle of electrochemical voltage spectroscopy: a) potential program, b) corresponding recorded current decay and c) plot of ΔQ/ΔE vs. E after integration.

state (Fig. 2b). After a certain time for equilibration the potential is stepped to $V + 2\mathrm{d}V$ and the process is repeated. The potential is stepped in this way to some maximum value and back to the initial point. For our experiments a step width of 10 mV and a waiting time of 1 min was used. After integration of each step over time values of ΔQ are obtained, which express the amount of accumulated charges during each potential step. The plot of ΔQ/ΔE vs. E (Fig. 2c) can then be interpreted as an 'infinitesimal slow' CV.

In situ UV-VIS spectroelectrochemistry was carried out inside a glovebox using an Avantes AVS-USB2000 Fiberoptic Spectrometer. In this case the WE was a gold grid evaporated on a glass plate.

In situ IR spectroelectrochemistry was performed in attenuated total reflection geometry [9] with a germanium reflection element as WE. Measurements were performed on a Bruker IFS 66/S FTIR spectrometer.

Absorption measurements were done using the Avantes AVS-USB2000 Fiberoptic Spectrometer both at room temperature and with He cooling. All samples were dropcast from toluene solutions.

3. RESULTS AND DISCUSSION

Figure 3 shows the electrochemical data for PTPTB, comparing CV and EVS. Figure 4 shows the comparison of CV and EVS for MDMO-PPV. A delay of the dedoping process of the oxidation is observed both with CV and EVS. In EVS the dedoping process should theoretically be completed at the onset potential of oxidation for reversible processes. This indicates the

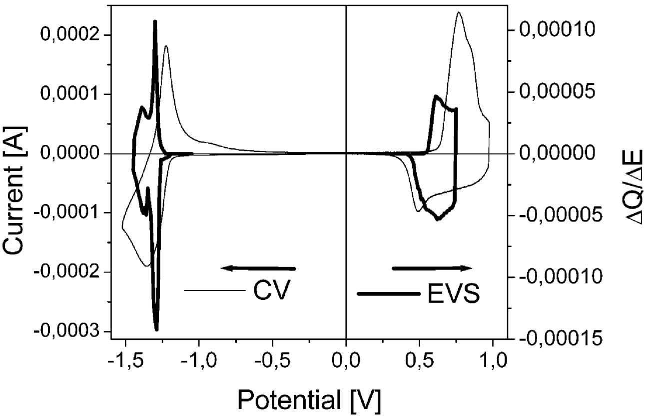

FIGURE 3 Electrochemistry of PTPTB: — CV at 10 mV/s, left scale, — EVS, right scale, onsets determined at +0.54 V and −1.2 V vs. Ag/Ag$^+$, $E^{1/2}_{\mathrm{Ferrocene}} = 420\,\mathrm{mV}$.

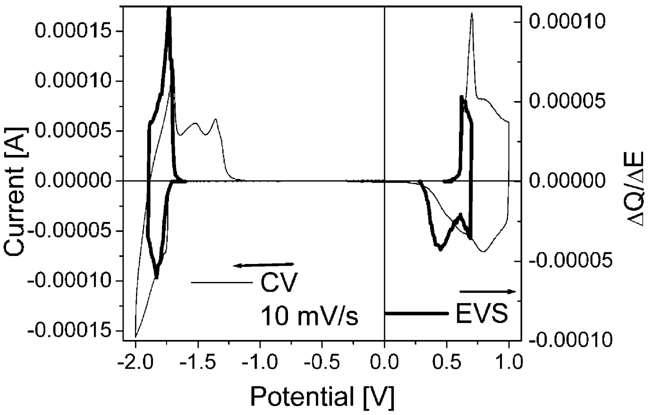

FIGURE 4 Electrochemistry of MDMO-PPV: — CV at 10 mV/s, left scale, — EVS, right scale, onsets determined at +0.55 V and −1.72 V vs. Ag/Ag$^+$, $E^{1/2}_{\text{Ferrocene}} =$ 420 mV.

non-ideality of these systems. From electrochemistry a bandgap of 1.8 eV for PTPTB and 2.3 eV for MDMO-PPV was obtained.

Figure 5 shows the absorption spectra of MDMO-PPV and PTPTB. The optical bandgap is determined with a tangential through the turning point of the low energy side of the spectra, leading to estimated values of 1.7 eV for PTPTB and 2.1 eV for MDMO-PPV. The absorption spectrum of PTPTB

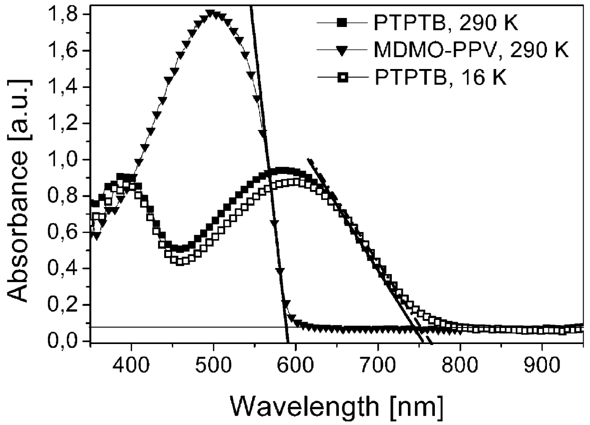

FIGURE 5 Absorption spectra of PTPTB and MDMO-PPV: determined bandgap of 1.7 eV for PTPTB and 2.1 eV for MDMO-PPV.

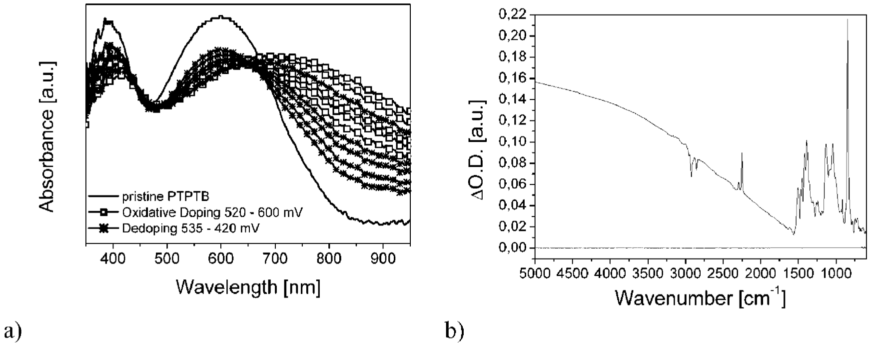

FIGURE 6 *In situ* spectroelectrochemistry of PTPTB: a) UV-VIS spectra during oxidative doping and dedoping, b) IR difference spectra with respect to the pristine material during oxidative doping.

at low temperature shows small changes in the maximum and a very small redshift (less than 50 meV).

The spectroelectrochemical data for PTPTB are depicted in Figure 6. In the UV-VIS absorption spectra in Figure 6a the evolution and decrease of a broad band around 800 nm assigned to a polaronic transition [6,10,11], is observed. From a correlation of the spectra to potential values, again a delay of the dedoping process for oxidation is obtained, as found with the EVS measurements (see above). Furthermore, we observed that the oxidation process is not completely reversible as the original spectrum is not recovered after dedoping. Either kinetic hindrence due to counter ions having to enter and leave the polymer during the redox process or chemical changes within the polymer upon oxidation can explain these observations.

In the IR spectrum in Figure 6b, recorded *in situ* during oxidation, a second polaronic transition as a broad band above $\sim 2000\,\text{cm}^{-1}$ is observed. At lower energies the infrared active vibration (IRAV) modes are evolving which are very characteristic and a prove for charges brought onto the polymer chain and stabilized there [12].

From the electrochemical and optical data, especially if the results are also confirmed by spectroelectrochemical results, a detailed overview on the electronic levels of the substances can be derived. Figure 7 shows a summary of the determined HOMO and LUMO levels, put in the energy diagram for an organic solar cell.

As can be seen, the HOMO's of PTPTB and MDMO-PPV are at the same position, while the LUMO of PTPTB is lower by 0.5 eV compared to that of MDMO-PPV. Due to the isoenergetic HOMO levels the similar open circuit voltages for a PTPTB:PCBM solar cell [7,13] as found in a MDMO-PPV:PCBM [1,14] cell can be explained. Photoinduced electron transfer to

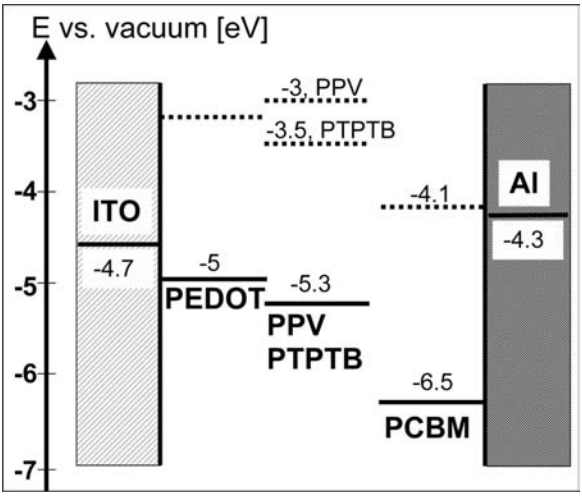

FIGURE 7 Energy diagram for an organic solar cell with the determined values for the HOMO ▬ and the LUMO ■ ■ ■ ■; values for PCBM taken from literature [13], for PEDOT value for "Baytron" from the Bayer company.

PCBM as the acceptor is energetically possible as there is still a difference of ~0.7 eV between the LUMO of PTPTB and that of PCBM.

Taking optical absorption, spectroelectrochemical and EVS measurements into account, a general prediction for photoinduced charge carrier formation can be made.

4. CONCLUSIONS

The bandgap MDMO-PPV has a value of ~2.2 eV and with a bandgap of 1.7–1.8 eV PTPTB can be considered as a low bandgap polymer. Similar values within ±0.2 eV of the electrochemically and optically determined bandgap were found for both materials. Our results show that using different methods the determined values also get more reliable. EVS is shown to be an appropriate method to determine the bandgap as well as the HOMO and LUMO levels of polymers. Together with spectroelectrochemistry a good prediction for redox suitability in combination with a known counterpart in a donor-acceptor tandem can be made.

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