

# Comparison of the electrochemical and optical bandgap of low-bandgap polymers

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## Abstract

The use of low bandgap polymers in organic photovoltaics for better light harvesting is getting more and more important. For determination of the electrochemical bandgap cyclovoltammetry (CV) and electrochemical voltage spectroscopy (EVS) was applied. The optical bandgap was determined by optical absorption measurements. The results are compared in terms of energy vs. vacuum level to predict the suitability of these materials for organic photovoltaics.

*Keywords:* low bandgap polymer, electrochemical bandgap, optical bandgap, cyclovoltammetry, electrochemical voltage spectroscopy

## 1. Introduction

In 'bulk-heterojunction' solar cells with power conversion efficiencies up to 3% [1–3] blends of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene], (MDMO-PPV) and 1-(3-methoxycarbonyl)propyl-1-phenyl-(6,6)C<sub>60</sub> (PCBM) are used. However, MDMO-PPV has a bandgap of around 2.2 eV, so for better light harvesting materials which absorb at photon energies at the maximum of the solar emission around 1.8 eV are getting more important. Therefore the determination of the width of the gap and the energetic positions of the band edges are important for these materials. In this contribution, we discuss methods for the determination of these parameters, which are necessary to predict energetic suitability for electron transfer to a fullerene unit. For this determination of the band edges and the gap EVS [4–6] in combination with absorption spectroscopy and in situ spectroelectrochemistry is applied. The results of the low-bandgap materials are compared with that of MDMO-PPV.

## 2. Experimental

The structures of the investigated low-bandgap materials are depicted in Fig. 1. UV-VIS in situ spectroelectrochemical measurements were performed with an Avantes AVS-USB2000 Fiberoptic Spectrometer. Electrochemical measurements were carried out at room temperature in a glovebox using a Jaissle potentiostat computer controlled with SCADA software. The supporting electrolyte was 0.1 M (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> in acetonitrile, the working and the counter electrode were platinum foils. The reference electrode (RE) was a silver wire coated with AgCl. In the EVS method the electrode

potential was varied in 10 mV-steps covering a range of 400 mV around the expected onset of oxidation and reduction, respectively. After each step the potential was kept constant for 1 minute to attain quasi-equilibrium conditions. If oxidation or reduction takes place, an abrupt increase of the current is observed. While the potential is kept constant, this current decays to the baseline until no more charges can be injected into the polymer at that certain potential. Integration of this data over time gives the change of the injected charges with the potential  $\Delta Q/\Delta E$ , which can be plotted vs. E and can be interpreted as an infinitesimal slow CV.

## 3. Results and discussion

Fig. 2 shows the absorption spectra of MDMO-PPV and PTPTB. From these measurements the optical bandgaps were determined from the tangentials as drawn in the plot,

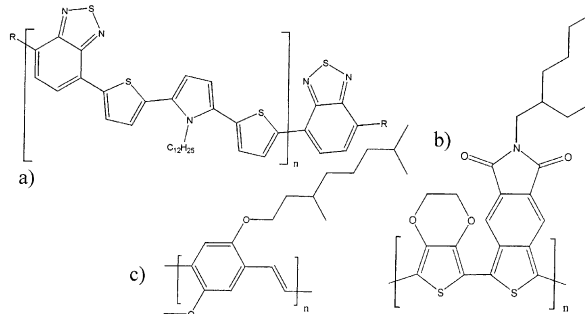


Fig. 1: a) poly-(*N*-dodecyl-2,5-bis(2'-thienyl)pyrrole-(2,1,3-benzothiazole)) (PTPTB, R = H, Br, n = 1–4) [7], b) Poly-(3,4-ethylene-dioxy-thiophene)-*N*-(2-ethylhexyl)-dicarboxylic-imide-benzo-[c]thiophene (PEDOT-EHI-ITN) [8], c) MDMO-PPV

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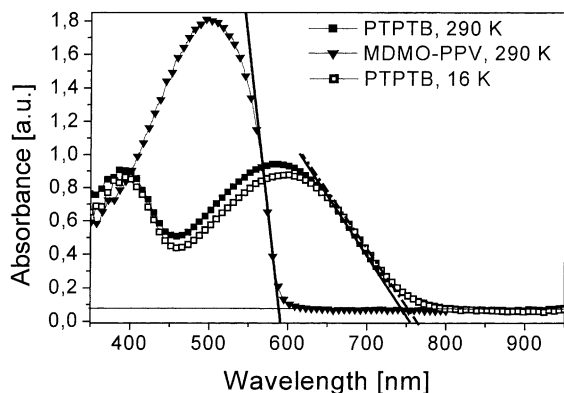


Fig. 2: Absorption spectra on films of PTPTB and MDMO-PPV; determined bandgap of 1.7 eV for PTPTB and 2.1 eV for MDMO-PPV, films dropcast from toluene solution

leading to values of 1.7 eV for PTPTB and 2.1 eV for MDMO-PPV. For PEDOT-EHI-ITN a value of 1.1 eV was taken from literature [8].

In Fig. 3 the EVS measurements of all three materials are depicted. The potential range around the onsets was determined by CV before. For the electrochemical bandgap the values for MDMO-PPV and PTPTB are 2.3 eV and 1.8 eV, respectively. These values are in good correlation with the optically determined bandgap. PEDOT-EHI-ITN shows a difference of only 0.5 eV for the onsets of oxidation and reduction, which is less than the half of the optical bandgap.

Fig. 4 shows the correlation of UV-VIS spectra obtained from in situ measurements with the potentials during an EVS experiment. The bleaching of the absorption band of the conjugated chain for oxidation and reduction starts at +90 mV and  $-1.1$  V, respectively. An electrochemical bandgap of 1.2 eV is obtained, which is in similar agreement to the optical measurement as for the other materials. Obviously electrochemical side reactions occur, which give unwanted contributions to the EVS signal. The result suggests that combined EVS and in situ spectroelectrochemical measurements should always be done for confirmation of the EVS data.

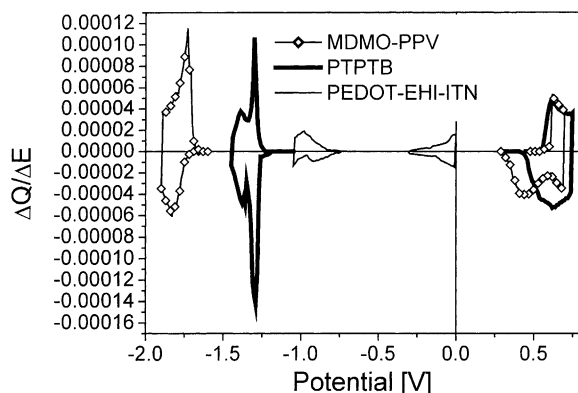


Fig. 3: EVS data of the polymers: Onsets for PTPTB are +0.54 and  $-1.2$  V, for PEDOT-EHI-ITN  $-0.29$  and  $-0.75$  V and for MDMO-PPV +0.55 and  $-1.72$  V vs. NHE; dropcast films on Pt

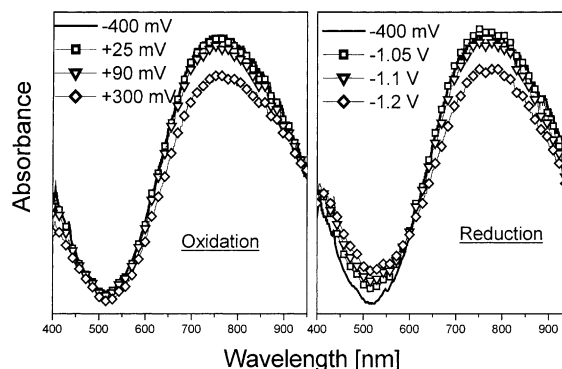


Fig. 4: In situ UV-VIS spectra of PEDOT-EHI-ITN during oxidation and reduction done with EVS: onsets for these reactions are +90 mV and  $-1.1$  V; dropcast films on Au-grid

The HOMO levels for PTPTB and MDMO-PPV are at nearly the same position at  $-5.3$  eV vs. vacuum level (assuming the normal hydrogen electrode at  $-4.75$  eV vs. vacuum). The HOMO for PEDOT-EHI-ITN was found at  $-4.9$  eV vs. vacuum. All LUMO levels are lying high enough (MDMO-PPV:  $-3$  eV, PTPTB:  $-3.5$  eV, PEDOT-EHI-ITN:  $-3.7$  eV, all vs. vacuum) to allow electron transfer to the LUMO of a fullerene acceptor unit ( $\sim -4$  eV) after light excitation.

#### 4. Summary

EVS is shown to be an appropriate method to determine the bandgap as well as the HOMO and LUMO levels of polymers. Corresponding values within  $\pm 0.2$  eV of the electrochemically and optically determined bandgaps were found. The combination of different methods like EVS – in situ spectroelectrochemistry gives more reliable results.

#### 5. Acknowledgements

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