Exchange grant University of Hasselt-University of Groningen

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Purpose of the visit

Conjugated polymers continue to attract considerable attention as a result of their promising properties for optoelectronic applications such as light emitting diodes,[1] solar cells,[2] sensors[3] and field effect transistors.[4] Whereas for selected applications suitable conjugated polymers are available, the quest for materials with improved properties continues. In this context, we have synthesized several promising new conjugated polymers, such as dodecyl-poly(fluoranthene vinylene) (**dodecyl-PFV**), poly(bis-octylphenyl-thienylene vinylene) **DOP-PTV** and **pBuAc-PPV-pBuAc** a triblock copolymer (Figure 1). **Dodecyl-PFV** is an n-type conjugated polymer, such polymers are quite rare and highly desired for solar cell application to potentially replace small molecule materials such as PCBM. The observed unusual n-type behavior originates from the non-alternant polycyclic aromatic hydrocarbon units in the backbone. **PTV** is a promising low bandgap donor material with a high hole mobility. **pBuAc-PPV-pBuAc** is a triblock copolymer that contains both conjugated, Poly (Phenylene Vinylene) and nonconjugated, Poly (Butyl Acrylate), segments.

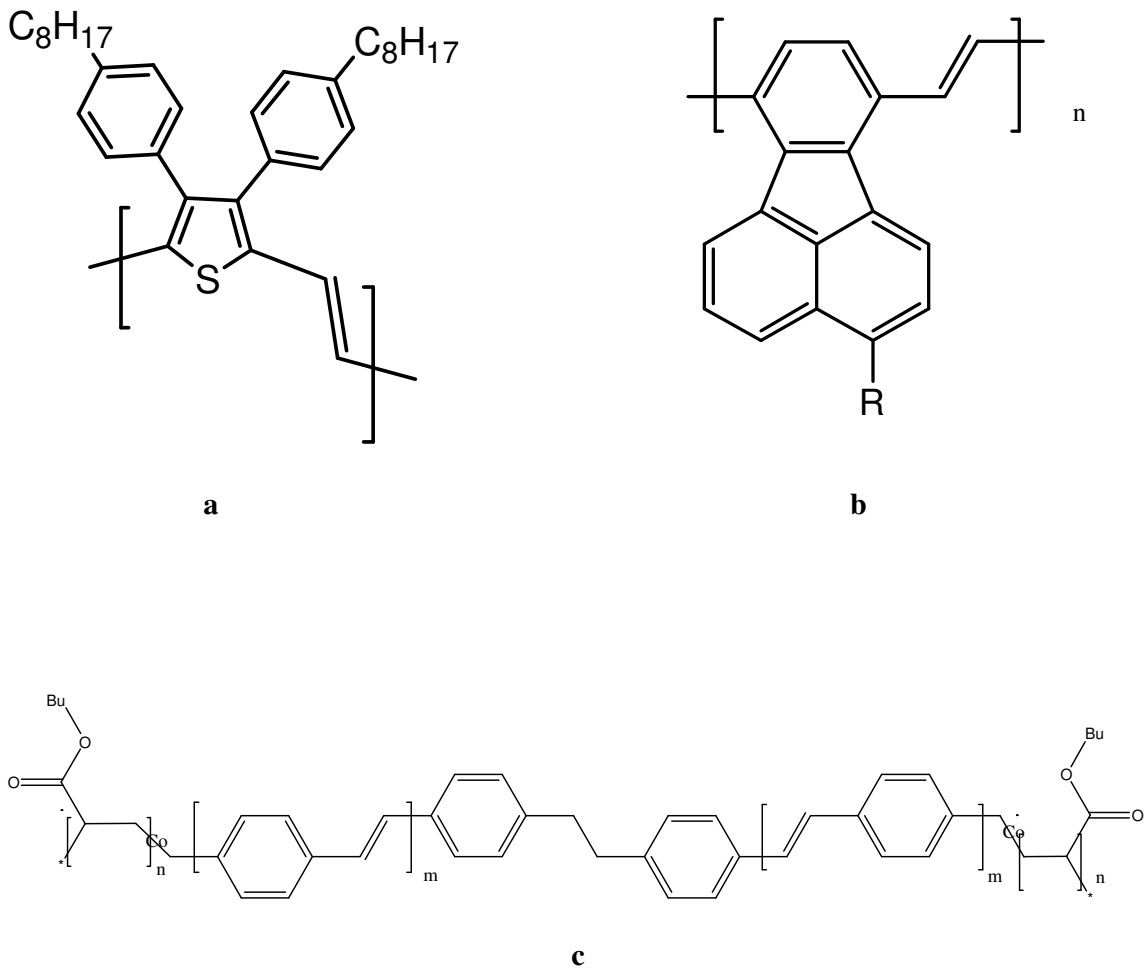

Figure 1. Chemical structures of a) poly(bis–octylphenyl-thienylene vinylene) **BOP-PTV** and b) dodecyl-poly(fluoranthene vinylene) **dodecyl-PFV.**

The aim of the visit was the study of charge transport and the fabrication of devices as solar cells and LED's as well with these interesting materials.

Description of the work carried out during the visit

Dodecyl-PFV

Dodecyl-PFV was tested at LIOS (Linz Institute for Organic Solar Cells) in Austria. We determined the electron mobility by CELIV ("Charge Extraction in a Linearly Increasing Voltage"). **Dodecyl-PFV** exhibits an electron mobility of 1.4 10^{-8} m^2/Vs. Hence it can be concluded that dodecyl poly(*p*-fluoranthene vinylene) is a promising material for organic solar cell applications. In this context it is noteworthy that the electron mobility reported in literature for PCBM is $\mu_e = 2 \cdot 10^{-7}$ m^2/Vs, which is only one order of magnitude larger than found for unoptimized thin films of **dodecyl-PFV**.[5] The high electron mobility confirms that this novel class of polymers holds significant promise for the application in solar cells. In this context it is noteworthy that preliminary experiments indicate that indeed organic solar cells can be obtained using **dodecyl-PPV** as the n-type material as a replacement of PCBM, although further optimizations are needed.

DOP-PTV

One of the main problems in polymer:fullerene solar cells is the poor overlap between the solar spectrum and the absorption of the used materials (Figure 2). In order to increase the photon harvesting, low bandgap polymers offer significant advantages.

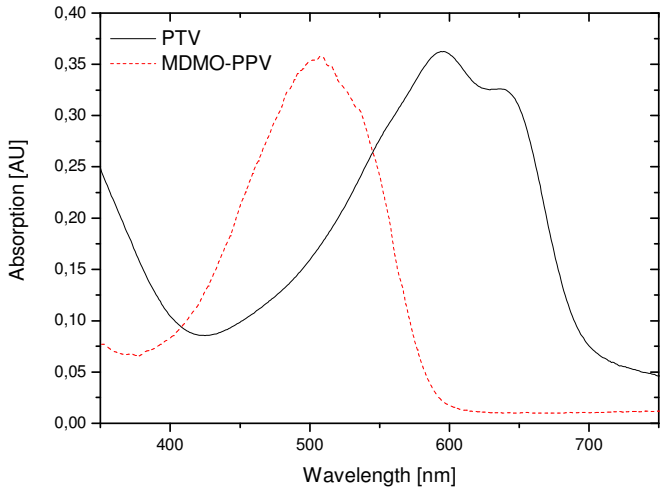

Figure 2. Absorption profile of a thin film of **DOP-PTV**, as compared to MDMO-PPV.

Previous studies have shown PTV to be a suitable material as a low band gap donor for polymer : fullerene solar cells. These studies however used a precursor route since the used PTV was insoluble. Here we use a soluble PTV from which we expect higher power conversion efficiencies due to the better processing capacities. Besides suitable energy levels this new donor material should posses appropriate charge carrier transport properties. To test whether this is the case hole only devices have been made resulting in a hole mobility of 3 x 10^{-9} m^2/Vs which is slightly lower as compared to P3HT, but nevertheless encouraging when compared to other novel low band gap donors (Figure 3). Combined with a the good transport properties of PCBM no space charge effects are expected, at least for moderately thick films, similar to those used in MDMO-PPV:PCBM blends.

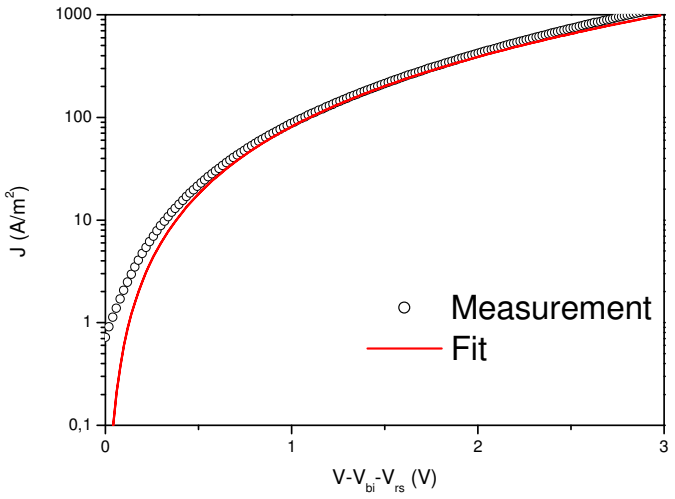

Figure 3. Current density versus voltage, corrected for built in voltage and series resistance of a **DOP-PTV** hole only device. Data (symbols) is fitted (solid line) using a space charge limited current with a field dependent mobility.

First experiments show encouraging results with high open circuit voltages (Voc) of 0.67 V and fill factors of 60% and higher for films with a thickness of more than 200nm, indicating good charge transport properties of the blend. The short circuit currents (Jsc) however are still inferior compared to model systems resulting in somewhat low efficiencies (highest achieved thus far ~ 0.8%). We believe optimizing the morphology of the blend will result in higher currents and hence efficiencies (Figure 4 and Table 1).

	Voc (V)	**Jsc (A/m^2)**	**Efficiency (%)**
1:1 DOP-PTV:PCBM	0.66	9.1	0.34
1:2 DOP-PTV:PCBM	0.67	15.8	0.66
1:4 DOP-PTV:PCBM	0.67	18.3	0.80

Table 1. Solar cells performance for different ratios **DOP-PTV**:PCBM.

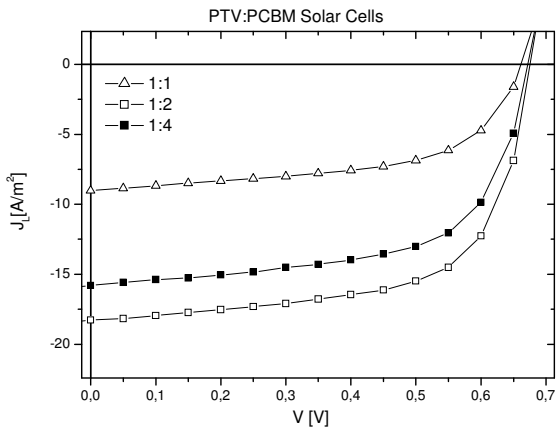

Figure 4. Current density versus voltage of selected **DOP-PTV**:PCBM solar cells under illumination of a 1000 W/m2 simulated solar spectrum.

pBuAc-PPV-pBuAc

Light emitting diodes were fabricated by sandwiching this block co-polymer in between a ITO/PEDOT:PSS anode and barium/aluminum cathode. Since it appeared that the conjugated polymer was insoluble in all common organic solvents tested. The thin film was prepared in the precursor stadium and thermally converted afterwards. Figure 5 shows the current density versus applied voltage characteristics of a **pBuAc-PPV-pBuAc** LED with an active layer thickness of 100 nm. The device shows good diode characteristics and high currents at forward bias indicating good charge carrier transport properties.

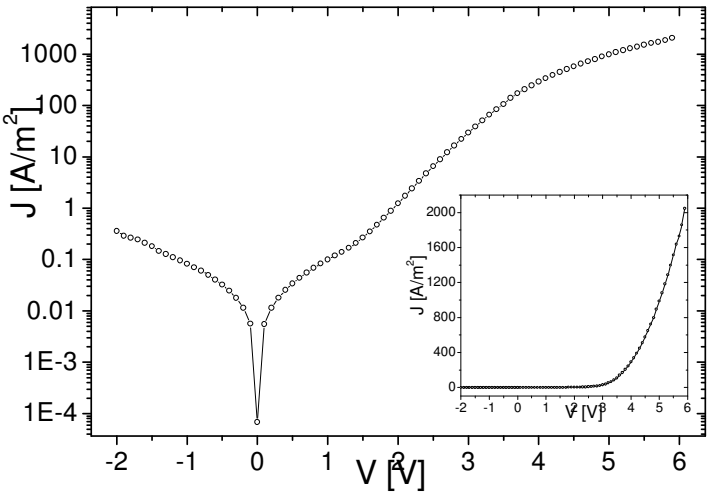

Figure 5. J-V characteristics of a pBuAc-PPV-pBuAc LED on a semi logarithmic and linear (inset) scale.

- In order to asses the **charge carrier mobility** of the polymers hole single carrier devices were fabricated using palladium as an electron blocking top contact.

pBuAc-PPV-pBuAc. As expected for a PPV type polymer the currents of the LED match the currents in a hole only device showing holes to be the dominant charge carrier in the material. The hole only device is fitted with a space charge limited current (see Figure 6) resulting in a zero field mobility of 4×10^{-9} m^2/Vs and a field activation coefficient of 2×10^{-5} $(V/m)^{-1/2}$. Such high hole mobilities are remarkable considering the relatively low mobility of pure PPV, a zero field mobility of 5×10^{-11} m^2/Vs and the fact that a large fraction of the copolymer is not conjugated. An explanation for this might be that most of the transport is due to interchain interactions as has been observed in polythiophenes. The electroluminescence (EL) spectrum at various voltages is shown in figure 7. Green light emission with a maximum at 514 and 549 nm, and no dependence on the applied voltage.

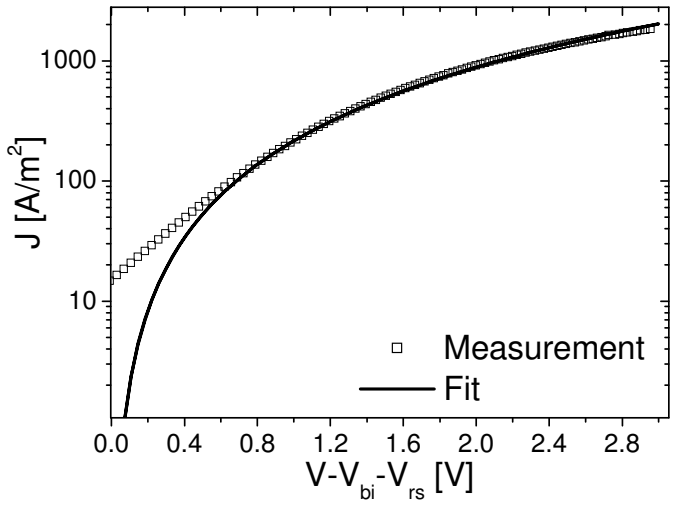

Figure 6. Current density versus voltage, corrected for built in voltage and series resistance of a pBuAc-PPV-pBuAc hole only device. Data (symbols) is fitted (solid line) using a space charge limited current with a field dependent mobility.

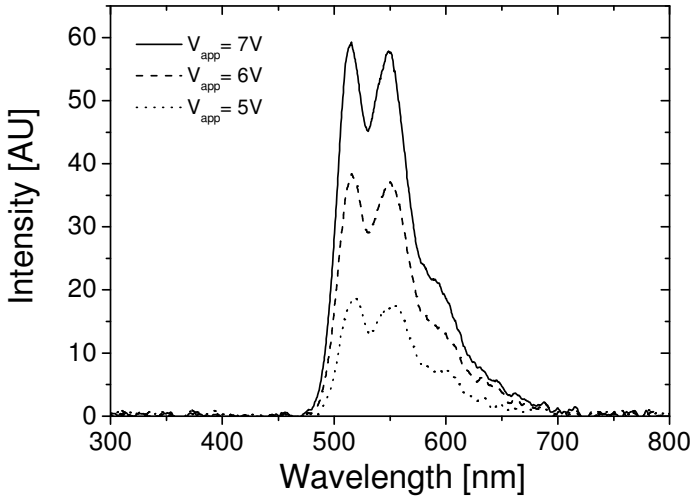

Figure 7: Electroluminescence spectrum of a pBuAc-PPV-pBuAc LED at different applied voltage.

The high hole mobility of the triblock co-polymer is remarkable considering to the relatively low mobility of pure PPV and the fact that a large fraction of the copolymer is not conjugated. This block co-polymer is no longer soluble in its conjugated form. For this reasons this block co-polymer is a very promising candidate to use as an hole transport layer in a LED, this can improve the light emitting characteristics.

Description of the main results obtained

-The high electron mobility of C12-PFV confirms that this novel class of polymers holds significant promise for the application in solar cells.

- Previous studies have shown that this new PTV-derivative is a promising low band gap material for polymer : fullerene solar cells.

-The green light emitting copolymer pBuAc-PPV-pBuAc has a better hole mobility than pure PPV.

Future collaboration with host institution

Based on the exciting results so far, I will have certainly benefit from my extended stay in the Zernike research group for molecular electronics of Prof. Paul Blom and Prof. Bert de Boer until the end of July. This prolonged stay would most likely leads to results that will find their way into several publications.

Projected scientific publications resulting from your exchange grant

1. Poly(p-Fluoranthene Vinylene) and its Derivatives: a Universal Synthesis Route towards Novel Electron Accepting Conjugated Polymers for Organic Solar Cell Applications, submitted to Macromolecules soon
2. Green light emitting copolymer with both conjugated and non-conjugated segments, submitted to Chem. Com. soon