

# Organic thin-film photovoltaic cells based on low gap thiophene oligomers

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## Abstract

*The best polymeric solar cells reported so far are based on a so called bulk heterojunction of polythiophene as a donor and a soluble fullerene derivative as an acceptor. However, these cells still suffer from an unsatisfying photovoltage typically below 0.6 V. Here, we show that we can achieve higher photovoltages using a new thiophene based oligomer comprising electron withdrawing groups that increase both the ionization energy and even more strongly the electron affinity of the compound. The new material is tested in MIP-type cells using a photoactive heterojunction to separate the excitons generated in the oligomer and a p-doped wide-gap transport layer. First solar cells show an open-circuit-voltage of above 0.8 V, fill factors around 50 % and a broad spectral sensitivity band starting at 650 nm. Solar cells based on such thiophene oligomers have the potential of high power efficiencies up to 3 % and are promising candidates for stacked PIN-type organic solar cells tailored to the sun-spectrum.*

We investigate a new organic material-class consisting of a thiophene based oligomer comprising electron withdrawing groups that increase both the ionisation energy and even more strongly the electron affinity of the compound.

The material which is presented here comprises three thiophene monomer units and is therefore called LG3T (low gap ter-thiophene) in the following. The absorption-spectrum of a dilute solution of LG3T in CH<sub>2</sub>Cl<sub>2</sub> as plotted in figure 1 shows a broad peak at 500 nm. The spectrum of a 30 nm thick vacuum deposited LG3T-layer is red-shifted, broadened and shows a subpeak structure which might be interpreted as a vibronic structure. For polythiophenes, such behaviour is commonly understood in terms of a coplanarization of the thiophene rings enforced by the crystal structure. Figure 1 also shows the photoluminescence of the LG3T-layer. The red shift of absorption in the solid state together with the low shift between the absorption edge and the luminescence peak points towards a close pi-stacking of planarized molecules with a stacking axis being strongly tilted with respect to the normal of the molecular axis to favour head-to-tail coupling of the transition dipoles similarly to the situation in J-aggregates.

For a possible use of LG3T on tandem cells in combination with phthalocyanine (ZnPc) based cells, it is remarkable that the absorption of the LG3T nearly perfectly fills the spectral gap of ZnPc around 550 nm.

The organic solar-cells are prepared using the materials C<sub>60</sub> as an electron acceptor and electron transport material, N,N,N',N'-Tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD) as an electron donor with wide optical gap (3.1 eV) as matrix for p-doped hole transport layers. As p-dopant, NDP2 provided by Novaled GmbH, Dresden, was used. The individual layers were deposited by thermal evaporation in a multiple-chamber UHV system on ITO-coated glass substrates with a surface resistance of 20 Ω/square. The I – V-characteristics were carried out in a glove box (N<sub>2</sub> atmosphere). Illumination is provided by a sun-simulator (Hoehnle) with an intensity of 127 mW/cm<sup>2</sup>.

As a first step, we prepared a flat heterojunction organic solar-cell with M-i-p-type structure with 20 nm LG3T as photoactive material and 5 nm MeO-TPD as donor-material, followed by 40 nm p-doped MeO-TPD, a 10 nm-thin contact layer of p-doped ZnPc and the final gold electrode. To stabilize the thin gold-electrode, we additionally deposited a layer of 80 nm aluminium on top. The I – V-characteristics are shown in figure 2 as curve **A**. The sample shows a short-circuit-current (J<sub>SC</sub>) of 4.4 mA/cm<sup>2</sup>, a fill-factor (FF) of about 0.39 and a high open-circuit-voltage (U<sub>OC</sub>) of 0.80 V. The weak dependence of photocurrent on backward bias indicates that we are dealing with a photoactive donor-acceptor-heterojunction rather than with a Schottky-type junction, i.e. the excitons formed in the LG3T are dissociated into a hole on MeO-TPD and an electron on LG3T at the

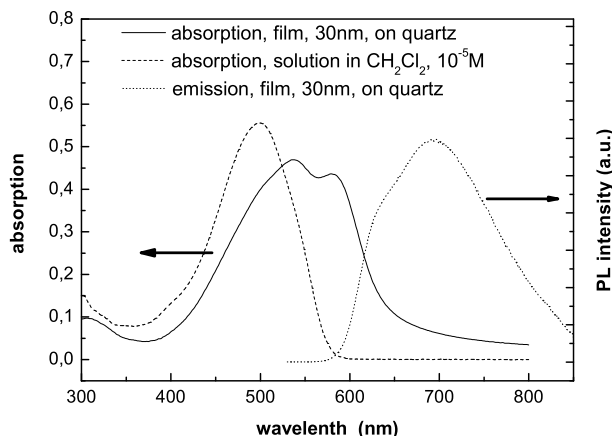


Figure 1: Absorption of LG3T in solution (dashed line) and of a 30 nm solid layer (solid line). Also the photoluminescence of this 30 nm layer is shown (dotted line).

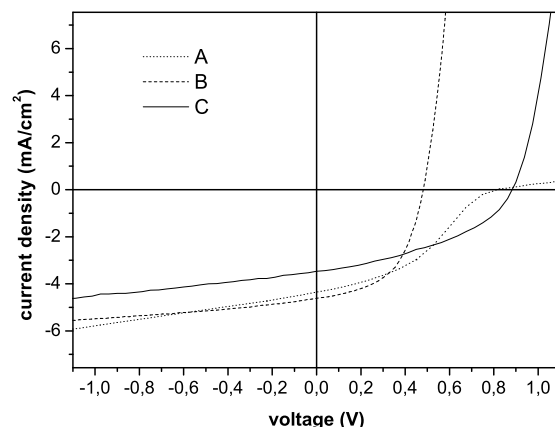


Figure 2:  $I-V$  characteristics of Mip-type cells with the layer sequence ITO/ photoactive layers (PAL)/ 5 nm MeO-TPD/ 40 nm p-MeO-TPD/10 nm p-ZnPc/5 nm Au/80 nm Al where PAL is: A: 20 nm LG3T; B: 5 nm  $C_{60}$ /30nm  $C_{60}$ :LG3T (2:1); and C: 5 nm  $C_{60}$ /30nm  $C_{60}$ :LG3T (2:1), respectively.

organic heterointerface. Due to its increased electron affinity, the thiophene-oligomer acts as an acceptor and electron transport material here. The short-circuit-current being pretty high for a flat heterojunction indicates a high exciton-diffusion length in LG3T. The low current in forward direction is a hint for a non-ohmic-contact behaviour for electron injection from the ITO into LG3T.

To improve injection and transport of electrons, we prepared a sample **B** with an additional 5 nm thick electron injection layer of  $C_{60}$  and a 30 nm blend layer of  $C_{60}$  and LG3T with mixing ratio of approximately 2:1 by weight instead of the pure layer. However, this blend does not form a donor-acceptor bulk heterojunction because the two blended materials have roughly the same ionization energy. Nevertheless, this sample reaches a  $J_{SC}$  of 4.6 mA/cm<sup>2</sup> and the FF improves to 0.53 while  $U_{OC}$  decreases to 0.48 V. The explanation of this behavior is as follows: The excitons on the LG3T are transferred to a singlet-exciton-state on the  $C_{60}$  by energy-transfer. This is also indicated by the total quenching of the LG3T fluorescence signal in these blend layers. On the  $C_{60}$  molecules, the singlet-excitons undergo inter-system-crossing to the triplet-state which is known to be very efficient in  $C_{60}$ . At this point, it is still questionable, if the triplet-excitons are transferred back to the LG3T. Nevertheless, these triplet excitons can diffuse in the blend to the MeO-TPD-interface where the dissociation into charge carriers takes place, so that a hole on the HOMO-level of the MeO-TPD and an electron on the LUMO-level of the  $C_{60}$  are formed. The free energy of the generated charge carrier pairs is lowered here as compared to sample **A** because the LUMO of  $C_{60}$  is lower than that of LG3T. Accordingly, we find a reduced value of  $U_{OC}$  which corresponds to simple heterojunction diodes of MeO-TPD and  $C_{60}$  prepared in our labs.

We also prepared a sample **C** with an additional thin pure interlayer of 5 nm LG3T between the blend layer and the donor-material MeO-TPD. The  $I-V$ -characteristics are plotted in figure 2. This sample shows again a much higher  $U_{OC}$  of 0.88 V. In contrast to sample **A**, however, it shows a reasonable fill factor and a good electron transport indicated by the high current in forward direction. Most interestingly, the photoaction spectrum of this sample still features a pronounced response upon excitations of  $C_{60}$  which can be rationalized as follows: Triplet-excitons are formed on the  $C_{60}$  of the blend layer just like in sample **B**. These triplet-excitons are obviously transferred back to LG3T which enables them to cross the pure LG3T interlayer and reach the MeO-TPD interface where free charge carriers are formed like in sample **A**. As electrons are generated on the high lying LUMO of the LG3T, we again observe a high photovoltage.

In conclusion, we have demonstrated solar cells based on blends of two acceptor materials, LG3T and  $C_{60}$ , where singlet excitons are generated mostly on LG3T, transferred to  $C_{60}$ , undergo inter-system-crossing on  $C_{60}$  and are transferred back to LG3T. The triplets on LG3T are long living and can diffuse to a photoactive interface to be separated into carrier pairs.