

Electrochemical characterization of polymer electron donors for organic solar cells

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K. Theodosiou*¹, S. Kakogianni², A. Andreopoulou², G. Leftheriotis¹, J. Kallitsis²

¹ Renewable Energy and Environment Laboratory, Dept. of Physics,

² Advanced Polymers & Hybrid Nanomaterials Research Laboratory, Dept. of Chemistry

University of Patras, 26500, Greece

email: krtheodosiou@upatras.gr



ΠΑΝΕΠΙΣΤΗΜΙΟ ΠΑΤΡΩΝ
UNIVERSITY OF PATRAS

Introduction

In recent years, significant research interest is targeted towards new types of low cost solar cells. Organic photovoltaics (OPV), based on conjugated polymers offer simplicity and low cost device fabrication. Efficiencies of OPVs received a major boost by the bulk heterojunction (BHJ) concept, consisting of an electron donor (conjugated polymer) and an electron acceptor (fullerene) material, blended together to give a disordered discontinuous network. However there are still problems to be solved, such as poor charge transport and low operational stability. A more efficient charge transport is achieved by alignment of the energy levels of the active materials. Suitable materials can be developed, tailoring the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the compounds.

In this report two highly promising materials belonging to the PCDTBT class were developed bearing different side and/or end substituents. Cyclic voltammetry was used for the determination of the HOMO and LUMO energy levels in order to retrieve initial indications of the polymeric derivatives' exact chemical structure and molecular characteristics [3] effect of onto the energy levels.

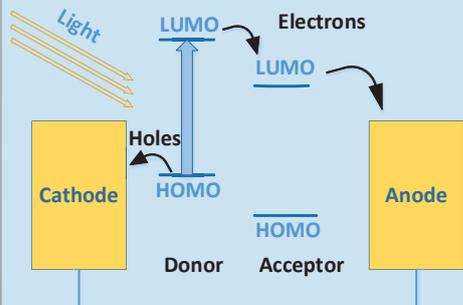
Operating Principle of OPVs

Generally, an organic solar cell operates through four steps:
✓ A photon is absorbed by the donor and an exciton (strongly bounded electron-hole pair) is produced.

✓ The exciton diffuses to the interface of the donor/acceptor materials.

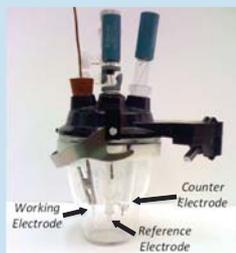
✓ The exciton is separated at the interface with the hole remaining in the donor phase and the electron diffusing at the acceptor phase.

✓ Finally, if continuous paths exist from the interface of each material to the corresponding electrode, the generated charge carriers will be transported to and collected at the electrodes.



Experimental

Cyclic voltammetry measurements were carried out with use of an Autolab electrochemical analyzer. A three electrode cell was used, consisting of a platinum wire counter electrode, an Ag/AgCl reference electrode and an ITO/Glass working electrode with the polymer to be measured drop-casted on the ITO conductive side. Films were deposited on preheated ITO at 80°C for 20 min. After deposition films annealed at 80°C for 15 min. As supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1M) was used. Before carrying out the measurements the cell was purged with pure argon gas for 20 min. Ferrocene was added to the mixture to calibrate the potential of the reference electrode.



Reference electrode: Ag/AgCl

Counter electrode: Pt wire

Determination of HOMO-LUMO energy levels

HOMO-LUMO energy levels as well as electrochemical band gap (E_g) were calculated by the following empirical relations with use of Fc level of -4.8eV [1,2]:

$$E_{\text{HOMO}} = -e(E_{\text{onset}}^{\text{ox}} - E_{1/2}^{\text{Fc}}) - 4.8 [eV]$$

$$E_{\text{LUMO}} = -e(E_{\text{onset}}^{\text{red}} - E_{1/2}^{\text{Fc}}) - 4.8 [eV]$$

$$E_g = e(E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{red}}) [eV]$$

where $E_{\text{onset}}^{\text{ox}}$, $E_{\text{onset}}^{\text{red}}$ are the oxidation and reduction onset potentials relative to Ag/AgCl electrode. The estimated redox potentials and the HOMO, LUMO energy levels are summarized in Table 1.

Table 1: HOMO/LUMO energy levels obtained from cyclic voltammetry.

Compound/Solvent	$E_{\text{onset}}^{\text{red}}$ (V)	$E_{\text{onset}}^{\text{ox}}$ (V)	E_g (eV)	HOMO (eV)	LUMO (eV)
P3.6C ^{EH} -DTBT-Ph (TCE)	-0.94	+0.95	2.0	-5.2	-3.2
P3.6C ^{EH} -DTBT-Ph (TOL)	-1.04	+1.16	2.2	-5.4	-3.2
P3.6C ^{OC} -DTBT-5F (CB)	-1.08	+1.10	2.1	-5.4	-3.3
P3.6C ^{OC} -DTBT-5F (TOL)	-1.16	+1.17	2.3	-5.4	-3.1

Cyclic Voltammetry

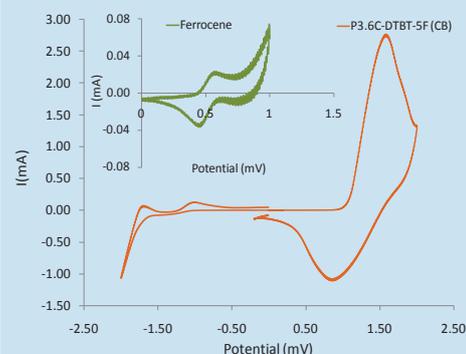


Figure 1. Cyclic voltammogram of P3.6C-DTBT-5F (CB), Scan rate 0.1V/s. Inset: Voltammetry of Fc.

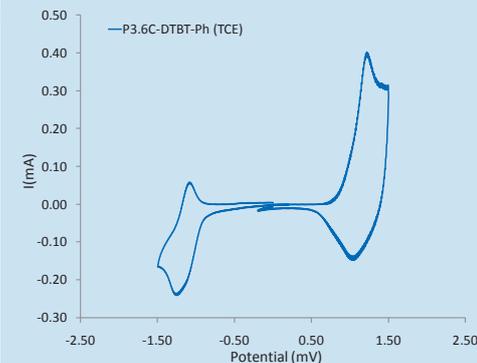


Figure 2. Cyclic voltammogram of P3.6C-DTBT-Ph (TCE), Scan rate 0.1V/s.

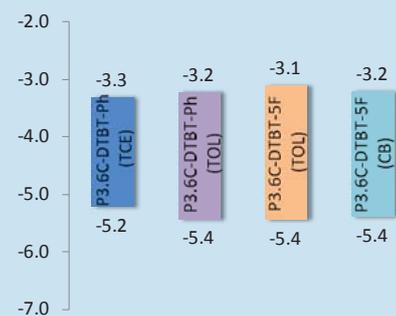


Figure 3. Energy level diagram of polymer compounds.

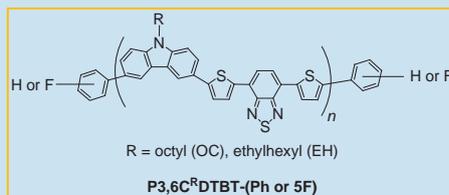
Semiconducting Polymers

PCDTBT is an electron donor-acceptor alternating copolymer based on sequences of carbazole and dithienylbenzothiazole monomers. It is an efficient and stable material for BHJ solar cells that surpasses the performances of P3HT, which is the most studied polymeric material until now [4].

The herein studied PCDTBT analogues were prepared by Suzuki coupling of the dibromo-dithienylbenzothiazole and of the 3,6-bis(boronic ester)-N-9'-octyl or ethylhexyl carbazole monomers. The polymeric chains were end-capped with phenyl or perfluorophenyl units in order to enhance the stability of the materials, to allow further functionalization and also to examine possible influence of these groups onto the electrochemical characteristics of the materials [5].

During the Soxhlet extraction and fractionation of the polymers, different solvents were used in the following order: acetone, toluene (TOL) and then 1,1,2,2-tetrachloroethane (TCE) or Chlorobenzene (CB). The toluene polymeric fractions have lower molecular weights (Mn~3kDa) compared to the TCE or CB fractions (Mn~6kDa).

General structure of the examined electron donor polymers



Acknowledgments

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Conclusions

- Successful preparation and electrochemical characterization of end-functionalized PCDTBT derivatives.
- The introduction of functional end-groups does not influence the energy levels.
- Lower molecular weight polymers (toluene fractions) showed slightly higher energy gaps than higher molecular weight ones (TCE or CB fractions).
- This work opens the way for the development of hybrid low band gap polymers for OPVs.