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**Study of a hole-conducting material addition to P3HT-PCBM bulk heterojunction
solar cells**

Final report

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This is the final report on the research activity that I carried out at the Linz Institute for Organic Solar Cells (LIOS, Austria) under the supervision of Prof. Niyazi Serdar Sariciftci, in the period from April 16th, 2010 to August 6th, 2010.

As reported in the research program that I submitted to the European Science Foundation, the experimental work that I performed during my 16 weeks visit at the LIOS Institute for Organic Solar Cells has consisted in the extensive characterization of an oligothiophene oligomer (PTO) that I synthesized previously in the Organic Chemistry laboratories of the Chemistry Department at the University of Bari, institution where I presently hold a position as Post-doc researcher.

The goals were:

1. To demonstrate that the oligomer is a suitable donor material for BHJ solar cells;
2. To demonstrate that addition of PTO to P3HT:PCBM bulk-heterojunction solar cells improves the overall efficiencies;
3. To characterize the oligomer electrochemically in order to detect the energy levels of its frontier orbitals (HOMO and LUMO)
4. To study deposition processes of PTO (electropolymerization, evaporation, spin coating etc)

My activity included the realization of a series of organic bulk heterojunction solar cells containing the oligothiophene material under investigation as donor material in combination with PCBM as acceptor and n-transporting material, or as third component in P3HT:PCBM solar cells. The use of standard materials such as P3HT and PCBM for the reference active layer allowed obtaining very useful information about the behavior of this oligomer in bulk-heterojunction organic solar cells. All the samples have been characterized in a dry environment by acquisition of their current-voltage characteristics in the dark and under illumination with a sun simulator (Air Mass 1.5). After that I focused on the electrochemical characterization of the material. I performed several experiments of cyclic voltammetry both on PTO solutions and on its thin films. Due to the oligothiophene nature of this material a poly(p-phenylenethiophene) polymer was formed during each experiment. Since the polymerization curves recorded during the experiments looked interesting, the polymer formed was characterized by cyclic voltammetry and spectroelectrochemistry. Indeed it showed electrochromism behavior switching from the fundamental to the oxidation state (turning its color from red to dark green-blue). The results of this last experimental part could be also compared to the results obtained from the same polymer synthesized by chemical methods in Bari. This last activity was performed after my visit and the results are now waiting for publication in a scientific paper.

During my visit I participated in an International Conference, the HOPV-2011 Conference, held in Assisi from 23rd to 27th May 2010. During this conference I presented a poster presentation, entitled "Improvement of P3HT-PCBM bulk heterojunction solar cells performances by addition of a thiophene phenylene oligomer", where I inserted an explicit acknowledgement to the European Science Foundation for the ORGANISOLAR Exchange Grant program. Please also note that I attached a pdf copy of this poster presentation to my final report.

I deeply benefited from my exchange visit to LIOS and I wish to sincerely thank the European Science Foundation for the opportunity that they gave me to visit such an eminent research Institution and to thank Prof. N. S. Sariciftci for accepting me as a visiting researcher and for supervising my research program.

First of all I had the possibility to characterize some material and to access a large number of instruments. I could exchange scientific opinions with other scientists with a major formation different from mine (I am an organic chemist and I could learn a lot from the physicists working at LIOS) and freely re-interpret their scientific approach from my “chemical” point of view. This resulted in a series of ideas for the future development of my research activity that I will briefly mention in the following report.

Furthermore, I learned a lot about instrumentation, and I am really glad that my **know-how** will be transferred soon to the University of Bari: once I was back to the Chemistry Department I collaborated to the acquisition of new instrumentation destined to the fabrication and characterization of organic devices that we are currently setting up and I am responsible of. Therefore I think that, beyond any publication that will come from these scientific results, some of the ESF goals have been fulfilled, especially in consideration of the profit that my improved knowledge on organic electronics has brought to the University of Bari.

Last but not least I grew from a human point of view, having the opportunity to work with people of different cultures in a very friendly environment.

Some details about the experimental results will be presented below; the discussion part will be mainly improved during the writing of future manuscripts for possible publication.

Sincerely,

Alessandra Operamolla

1. INTRODUCTION

1.1 P3HT:PCBM BHJ solar cells

The most understood polymer-fullerene combination for bulk-heterojunction solar cells is the P3HT/PCBM system. The highest efficiencies reached up to now are among 4-5%¹. In this case, the good performances that can be reached by these devices strongly depend on the morphology of the blend. Indeed the morphology is strongly influencing the carrier transport and recombination, which further on determines the solar cell efficiency.

Regioregular P3HT and PCBM show rather good miscibility, therefore the processability of the two materials together is very straightforward, and chlorobenzene (or dichlorobenzene) has been already elected as the best solvent because it is able to dissolve P3HT as well as PCBM at room temperature^{1,2}. After spin-coating a relatively homogenous composite film is usually formed in which little or no phase segregation is observed. These films usually have efficiencies below 1% under AM 1.5 conditions¹. To drive the phase segregation of the two materials into well developed and ordered pathways for the transport of carriers (bicontinuous domains) it is necessary to apply to these films an external variable, like heat or solvent vapor, to induce the crystallization of the polymer, therefore changing the morphology. The first technique for this post-production treatment that was proposed is based on thermal annealing³ and is still one of the best ways to improve the performance of a P3HT/PCBM bulk heterojunction solar cell. Heating the active layer to a temperature above P3HT glass transition temperature (110°C) allows the polymer chains to reorganize and the PCBM to diffuse within the film, forming a more thermodynamically favorable structure. Indeed P3HT possesses the unique feature to form ordered lamellar structures upon heating⁴ and this improves both its capacity to transport charges and its absorption of visible light that becomes red-shifted. Therefore the application of a post-production treatment becomes necessary to obtain organic solar cells with the highest power efficiencies.

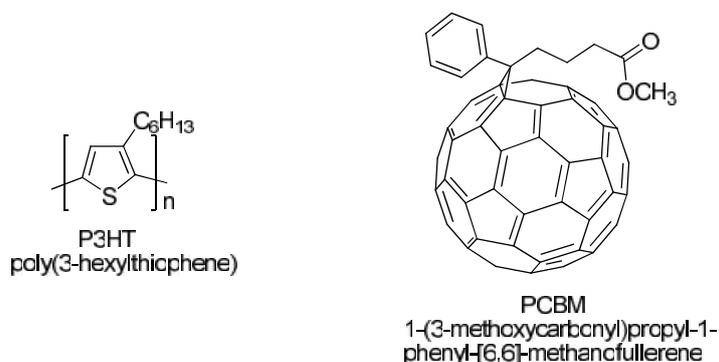


Figure 1. P3HT and PCBM chemical structures

1.2 Phenylene-thienylene based materials

Phenylene-thienylene based materials have revealed very good chemical and physical characteristics, such as solubility, adhesion for film formation, and electrical properties⁵. These rigid main chain materials containing lateral solubilising substituents, like the poly(2,5-dialkoxy-1,4-phenylene-alt-2,5-thienylene) (POPT), show some useful properties like solubility and fusibility that make them processable for a number of applications⁶.

The oligomer containing a dialkoxyphenyl core surrounded by four thiophene units, known as PTO, was employed as active layer in sensitivity enhanced field-effect chiral sensors, together with its two

biomolecule functionalized counterparts, PTA and PTG⁷ containing L-phenylalanine and D-glucosidic receptor moieties, respectively. As alkoxyphenylene-thienylenes are conjugated p-conducting systems⁸ also PTO shows this attitude. The Langmuir-Shafer processed bilayers of the PTO plus PTA or PTG were sandwiched between metallic contacts in an OTFT arrangement. These new bilayer sensing OTFTs are able to recognize some chiral flavors by showing field-effect amplified sensitivity that enables differential detection of optical isomers in the tens of parts per million concentration range.

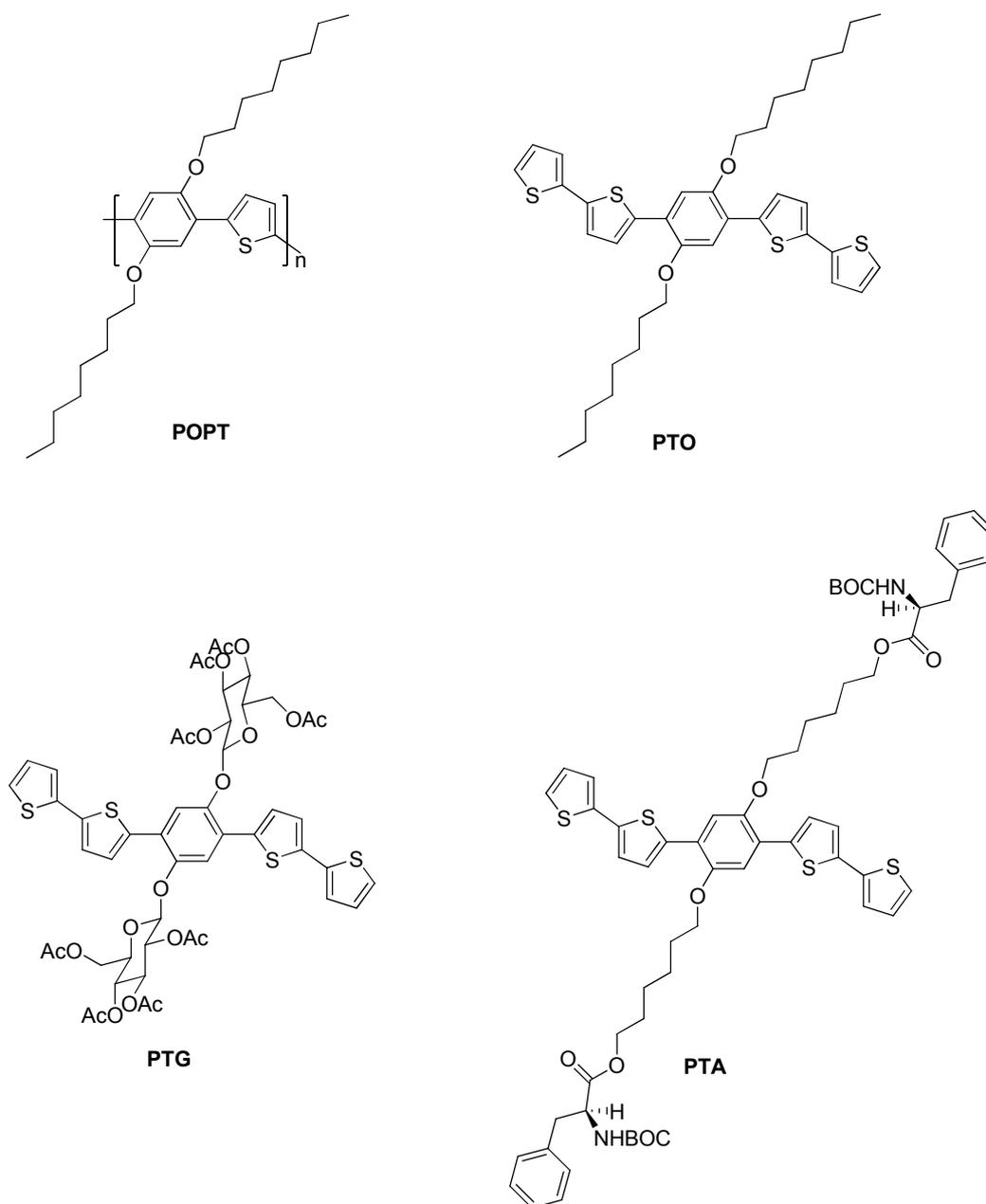


Figure 2. Structure of some phenylene-thienylene materials synthesized in Bari

1.3 Motivation of the work

PTO is a soluble oligomer that has shown some valuable characteristics as p-conducting material for organic field effect transistors. Its chemical structure, containing four thiophene units was tailored ad hoc for its application as a p-type organic semiconductor. Its solubility makes it very easily processable from solution and moreover it shows absorption of visible light in the green region of the spectrum. Given its structural

similarity to P3HT, it seemed an interesting topic to investigate the effect of PTO addition to bulk-heterojunction solar cells fabricated with regioregular P3HT and PCBM. The addition of this material to the active layer of this kind of devices is expected to influence their behavior as a consequence of different possible effects:

1. By influencing the layer morphology;
2. By influencing the layer absorption profile of visible light;
3. By influencing carriers mobility and/or recombination within the film;
4. By influencing the electric contacts between the layer and the metallic electrodes;
5. By enhancing carriers concentration generating more P3HT excitons by energy transfer from the excited state of PTO to the fundamental state of P3HT

2. Results and Discussion

2.1 Organic solar cells

The following figure 3 reports the absorption spectra in the solid state of the oligomer PTO and of its blend with PCBM. It is possible to notice that the oligomer PTO presents two absorption maxima at 432 and 462 nm in the solid state (green- blue region) and the blend of PTO and PCBM absorbs in the same region.

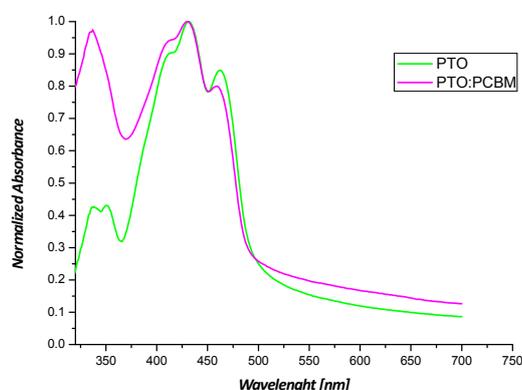


Figure 3. Solid state absorption of PTO and its blend 1:1 with PCBM

The solar cell fabricated with the p-conducting material PTO as the donor and PCBM as the acceptor gave the I-V characteristic reported in figure 4 and the performances reported in table 1. This cell shows a short circuit current density of 2.22 mAcm^{-2} , a fill factor comparable to the one obtained by the pristine P3HT:PCBM blend (see below) and a high V_{OC} , with a total efficiency of 0.6%. The same cell, when annealed with the same procedure employed before, loses its properties. The low efficiency of the pristine solar cell can be most importantly ascribed to the very low absorption of the active layer in the red region of the spectrum.

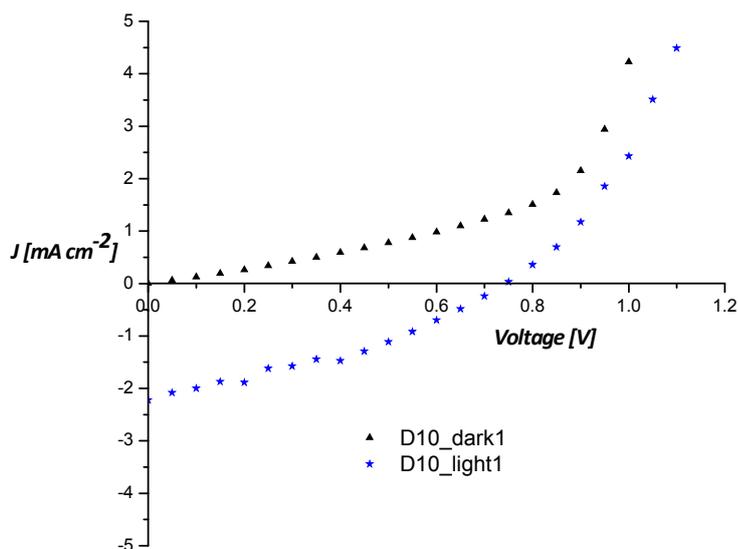


Figure 4. I-V characteristics in the dark and under illumination of PTO:PCBM as casted solar cells

Table 1. Performances of annealed and not annealed PTO:PCBM solar cells

Entry	Materials	Annealing	Jsc [mA/cm ²]	Voc [mV]	FF	Jmp [mA/cm ²]	Vmp [mV]	Efficiency η
1	PTO:PCBM	No	2.22	750	0.353	1.48	400	0.60 %
2	PTO:PCBM	yes	1.02	50	0.290	0.30	50	0.015%

Afterwards, a series of P3HT:PCBM bulk heterojunction solar cells containing small weight percentages of PTO with respect to P3HT (from 0.5% to 12.5%, 16 devices in total) were fabricated. Device performances start to improve when PTO:P3HT weight percentage is higher than 2%. The performances of some of these devices are summarized in the table 2 while the I-V characteristics under illumination of these devices in the fourth quadrant, in comparison with the characteristics of the P3HT:PCBM solar cell as processed and annealed, are shown in the figure 5.

Figure 5. I-V characteristics of solar cells prepared

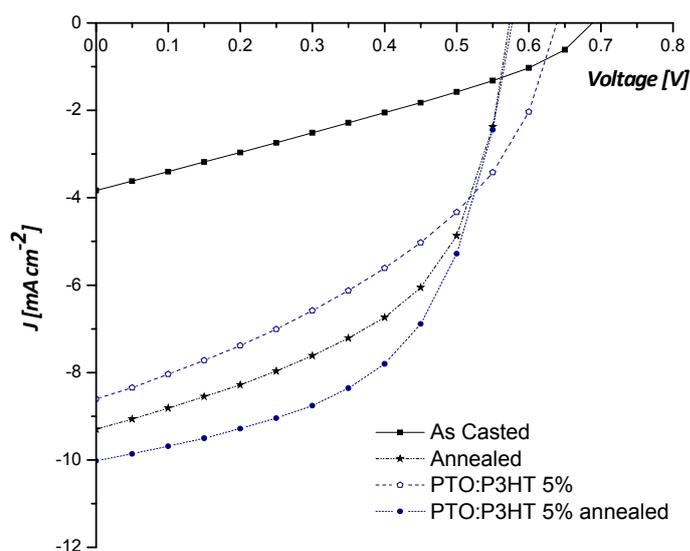


Table 2.

Entry	Materials	% PTO/P3HT	Annealing (110°C)	Jsc [mA/cm ²]	Voc [mV]	FF	Efficiency η
1	P3HT:PCBM	--	No	3.8	700	0.31	0.8%
2	P3HT:PCBM	--	Yes	9.3	550	0.53	2.7%
3	P3HT:PCBM Plus PTO	5%	No	8.2	650	0.42	2.2%
4	P3HT:PCBM Plus PTO	5%	Yes	10.0	600	0.52	3.1%

It can be observed that the addition of small amounts of PTO to the blend solutions prior to their deposition, has lead to the fabrication of devices having increasing values of the short circuit current densities, fill factors and efficiencies. Adding PTO increases the efficiency allowing to reach values of 3.1%. Another valuable observation involves the value of the V_{OC} , that for the devices fabricated with PTO maintains a higher value with respect to the sample obtained without additive and annealed.

UV-Vis absorption profiles and AFM studies do not evidence any noticeable morphology change by addition of PTO with respect to the P3HT:PCBM solar cells. Therefore it is possible to conclude that the percentage of the third material is low enough to influence in a negligible way the blend morphology but probably is able to improve the performance by other mechanisms such as energy transfer between the excited state of PTO and the fundamental state of P3HT, that need further study and clarification.

2.2 Cyclic Voltammetry

Cyclic voltammetry experiments (more than 30 experiments) were performed on PTO solutions and thin films both in acetonitrile and dichloromethane using gold or ITO as working electrodes and TBAPF₆ as

supporting electrolyte. During each experiment, precipitation on the working electrode of an insoluble polymer, whose structure is reported in the following figure 6, was observed.

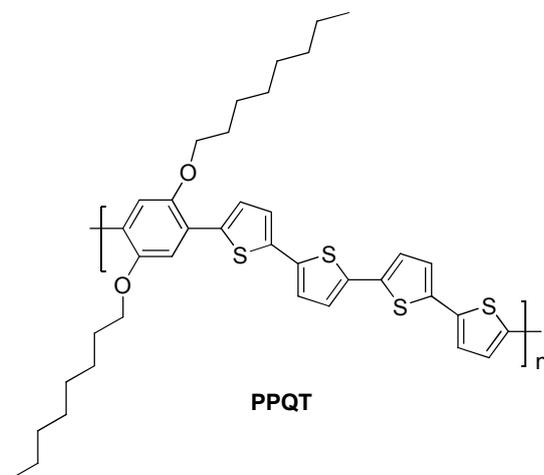


Figure 6. Chemical structure of the polymer formed

The polymerization curves detected using ITO as working electrode in 2.5 M dichloromethane solution are reported in the graph of figure 7. The second oxidation peak should correspond to the monomer oxidation observed in each cycle, while the first one, which appears from the second cycle on, should be due to the polymer. This last peak appears splitted in two shoulders: this does not necessarily indicate two oxidation states for the polymer but could simply be due to diffusion phenomena from the electrolyte solution.

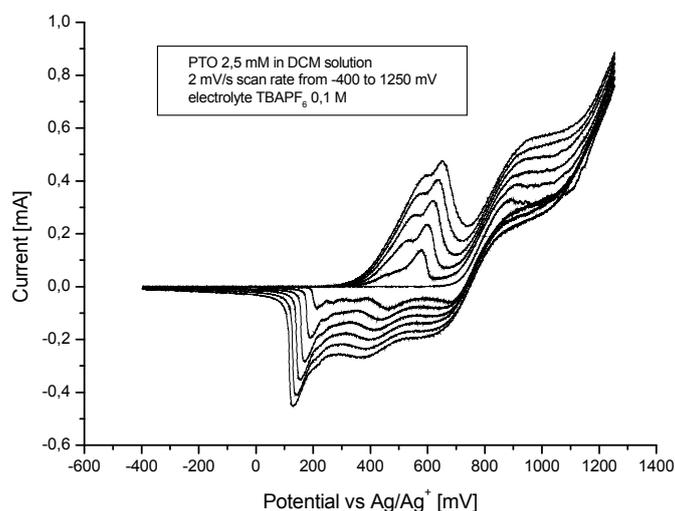
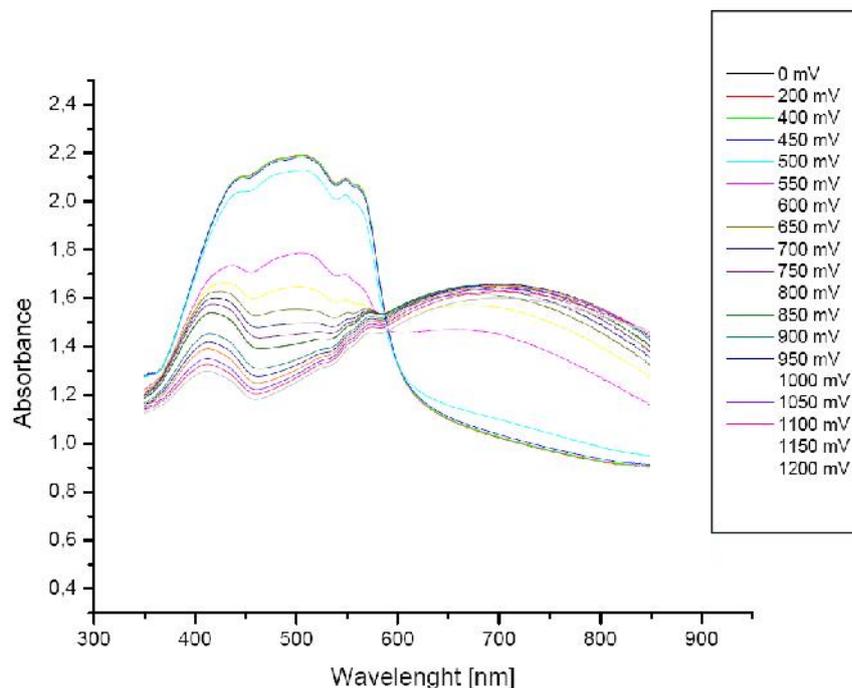


Figure 7

The polymer PPQT obtained in the previous experiments underwent spectroelectrochemical analyses by means of in situ electrochemical oxidation and detection of the UV-vis absorption spectra of the oxidized

state. The graph reported in figure 8 clearly shows that PPQT is an electrochromic material and its fundamental and oxidized states are colored in red and green-blue respectively.



3. CONCLUSIONS AND PLANNED EXPERIMENTS/PUBLICATIONS

In conclusion I performed the fabrication of BHJ solar cells containing P3HT and PCBM plus PTO in different weight percentages with respect to P3HT and their characterization in a modified environment. The I-V characteristics and the IPCE curves of the devices were acquired and compared to the absorption profiles of the blends. The electrochemistry of PTO was also studied and the formation of a new polymer PPQT was observed. This last material revealed to be an electrochromic material.

Some good results were obtained during this exchange visit. However some experiments are still required to publish these data. First of all more comprehensive morphological studies on PTO:P3HT:PCBM blends need to be performed. As far as the material PPQT is concerned, an investigation on the chemical synthesis of this polymer is currently in progress in Bari, because there are some issues concerning electropolymerized thiophene polymers that may negatively influence the polymer properties detected by spectroelectrochemistry. These issues are mostly relevant to cross-reticulation processes that may occur between thiophene rings connected to each other through β -linkages, which are usually generated by oxidation methods. Chemical syntheses performed by means of palladium catalyzed or activated reactions certainly do not introduce such uncertainty on the polymer structure.

Other open issues are relevant to the PPQT electropolymerized film morphological order: treatment of the surface with suitable ligands, i.e. formation of self-assembled monolayers on ITO or gold surface with molecules terminating with a thiophene ring, would certainly help to improve the order of PPQT films by

grafting the polymer chains on the surface instead of forming a disordered layer by simple precipitation of the polymer on the electrode during its formation.

Polymerization of the chirally substituted oligomers PTG and PTA is also an amenable development of this work: substitution of electrochromic polymers with chiral pending group would enable the study of the oxidized states of the deriving polymers by means of unconventional spectroscopic techniques such as circular dichroism: this would certainly open the way to intriguing new possibilities and discoveries in materials chemistry and physics.

Finally, thanks to this visit, the collaboration between the Chemistry Department of the University of Bari and the LIOS Institute (Linz) has been consolidated.

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IMPROVEMENT OF P3HT-PCBM BULK HETEROJUNCTION SOLAR CELLS PERFORMANCES BY ADDITION OF A THIOPHENE PHENYLENE OLIGOMER

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Introduction:

Bulk-Heterojunction organic solar cells (BHJ) offer great technological potential as a renewable source of energy (1). One of the last challenge in the preparation of these organic semiconductors based devices deals with the substitution of the thermal post-production treatment with the employment of some organic additives that are processed together with the donor and acceptor materials in the bulk heterojunction. The state of the art engages the use of alkyl thiols as co-solvents for the processing of polymer-PCBM solar cells (2). We have deeply investigated the influence of *n*-octylthiol additive on P3HT:PCBM BHJs and actually improvements of morphology, phase separation, light absorption and charges mobility were reported with respect to the corresponding untreated solar cell (3). Other studies on the employment of additives are concerning the use of small hole or electron conducting molecules, that are supposed to act on the recombination process or to influence the charges mobility. Such kind of additives have been employed on MEH-PPV:PCBM solar cells with slight improvement of the overall efficiency (from 0.02 to 0.24% by adding 40% of triphenylamine) (4), while addition of a third soluble hole conducting component to a blend consisting of P3HT:PCBM could enhance efficiency of a BHJ, provided that the third component is compatible with such materials (5).

AIM of the work:

In this communication we describe the use of a p-conducting phenylene-thiophene based material, PTO, as additive on P3HT:PCBM BHJs. PTO consists of an 1,4-dialkoxy-substituted benzene ring connected on the 2,5-positions to two dithiophene blocks (Figure 2).

PREVIOUS WORK ON PTO

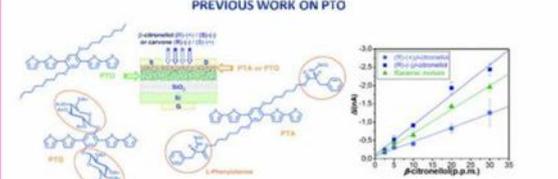


Figure 1. PTO, PTA and PTG in OTFT sensors: we have recently employed PTO and its small biomolecules functionalized counterparts, PTA and PTG, as active materials in a bilayer organic thin film transistor sensor that showed enantioselective recognition ability towards the citronellol and carvone enantiomers (6).

PRESENT WORK ON PTO

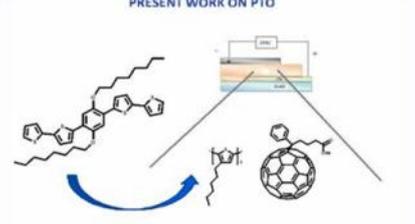


Figure 2 PTO as new additive on BHJs

Entry	Materials	% PTO/P3HT	Annealing (110°C)	Jsc [mA/cm2]	Voc [mV]	FF	Efficiency η
1	P3HT:PCBM	—	No	3.8	700	0.31	0.8%
2	P3HT:PCBM	—	Yes	9.3	550	0.53	2.7%
3	P3HT:PCBM Plus PTO	5%	No	8.2	650	0.42	2.2%
4	P3HT:PCBM Plus PTO	5%	Yes	10.0	600	0.52	3.1%

Table 1 Performances of the devices

The IV-characteristics (Figure 3) clearly show an increase of current density, fill factor and open circuit voltage by addition of PTO. The efficiency further increases up to 3.1% after thermal treatment of the cell. The efficiency of the cell with PTO after annealing is higher than the efficiency of the P3HT:PCBM solar cell annealed in the same conditions.

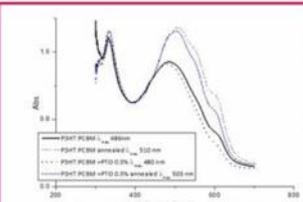


Figure 4 UV-vis absorption of the active layers

The UV-vis absorption spectra of the device with PTO does not show a clear red shift or the appearance of aggregation bands that are observed when *n*-octylthiol is used as additive. The annealing of this device produces similar effects in the UV-vis absorption as the annealing of the device containing P3HT:PCBM only. The AFM shows smooth morphology of the untreated BHJ containing PTO.

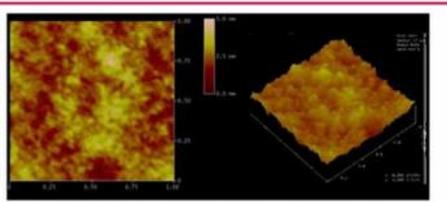


Figure 5 1µm x 1µm tapping mode AFM image of the not annealed PTO added solar cell

Conclusions

PTO is a new additive for P3HT:PCBM BHJs. Devices containing PTO display improved efficiencies and higher current densities. The effect of PTO on BHJs appears different from the effect of other additives like *n*-alkylthiols. These outcomes deserve deeper investigation, and studies on the comprehension of the mechanism behind the improved efficiency are in progress.

Acknowledgements

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