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Effect of Perylene as Electron Acceptor and poly(tetrabromo-p-phenylene Diselenide) as "Buffer Layer" on Heterojunction Solar Cells Performances

Alicia Godoy,[*1] *Linda Cattin,*[2] *Jean Christian Bernède,*[3] *Fernando Díaz,*[4] *Mará Angélica del Valle*[4]

Summary: Perylene derivatives, that behave as liquid crystal and might be used as electron acceptors, and poly(tetrabromo-p-phenylenediselenide) (PTBrPDSe) were synthesized with the purpose of using the polymer as buffer layer in solar cells. It was demonstrated that perylene compounds of N,N′-diheptyl-3,4,9,10-perylentetracarboxyldiimide (PTCDI-C7) and N,N′-diundecyl-3,4,9,10-perylentetracarboxyldiimide (PTCDI-C11) enabled obtaining photovoltaic effect when coupled with copper phthalocyanine (CuPc). The power conversion efficiency of the cells prepared from these perylenes is similar, whatever the x value. However this efficiency is smaller than the one achieved when the couple CuPc/C_{60} (fullerene) is used. More precisely, the best efficiency was obtained when a PTBrPDSe/Au buffer layer is introduced between the ITO anode and the CuPc. It was established that the presence of the thin PTBrPDSe layer allows improving the shunt resistance and consequently the cells performance.

Keywords: buffer layer; electron acceptor; organic solar cells; perylene; polymer

Introduction

Organic Photovoltaic cells (OPV cells) are more and more attractive as clean renewable energy source and have revealed promising potential as an alternative cheap energy source.[1]

Among these OPV cells heterojunction based devices are often used. Such structures are based on a couple of donor/acceptor layers (heterojunction). Often the donor is copper phthalocyanine and the acceptor fullerene (C_{60}). Although C_{60} is very efficient as electron acceptor it is also quite expensive while one of the main advantages expected for organic PV-cells is their low cost, therefore it would be interesting to work with cheaper acceptors.[2]

Perylene derivatives are promising compounds for application in electronic devices as molecular semiconductors. Actually, while most organic conducting materials can be described as p-type semiconductors (electron donors) perylene derivatives are usually described as n-type semiconductors (electron acceptors).[3,4] Such materials are potentially available as the electron-accepting material in all organic photovoltaic solar cells, as was reported in 1986 for the first solar based on a phthalocyanine and a perylenetetracarboxylic derivatives.[5,6] It has already been shown that increased ordering of perylenes molecules leads to an

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increase in exciton diffusion length.[7] Liquid crystals possess the ability of spontaneously self-organize into ordered structures, and N,N'-diheptyl-3,4,9,10-perylenetetracarboxylicdiimide (PTCDI-C7) is one of them.[8–11]

The purpose of this work was to synthesize and characterize perylene derivatives to study their likely application in solar cells. It is also noteworthy that introduction of a buffer layer between the anode and the organic material is quite useful.[12]

Improvement of organic solar cells performance has been accomplished using a zinc oxide anode coated by an ultra thin metallic layer.[13]

Polymers previously synthesized, such as poly(tetrabromo-p-phenylenediselenide)[14] have allowed the improvement of OLED results. This polymer is particularly temperature-stable and can be tested as "buffer layer" in our OPV.

Experimental Part

The synthesized compounds were characterized using ^{1}H-NMR carried out on a 200 MHz BRUKER ACP 200 instrument using TMS as reference. FT-IR spectra were recorded on a BRUKER VECTOR 22 spectrophotometer using KBr pellets. Elemental analysis was preformed on a C, H, N, S FISONS, Mod. EA-1108 analyser. Surface topography and film cross section were observed on a field emission scanning electron microscope (SEM, JEOL F-6400). Employing simple software the thickness of the films was measured from the cross section visualization. X-ray photoelectron spectroscopy (XPS) measurements (Leybold LHS12, University of Nantes-CNRS) were accomplished to investigate the coverage efficiency of CuPc thin films deposited onto the anode. XPS analyses were performed with a magnesium X-ray source (1253.6 eV) operating at 10 kV and 10 mA. During the measurements the vacuum was 10^{-7} Pa, the pass energy for high resolution spectra was 50 eV. The samples were grounded with silver paste to prevent charge effect.

A standard three-electrode glass cell was used for electrochemical characterization. All potentials quoted in this paper are referred to an Ag/AgCl electrode in tetramethylammonium chloride to match the potential of a saturated calomel electrode (SCE) at room temperature. A Pt gauze of large geometrical area, separated from the cell main compartment by a fine glass sinter, was used as counter electrode.

Electrical characterization of the PV-cell was preformed on an automated I-V tester, in the dark and under 1 sun global AM 1.5 simulated solar illumination.

PTCDI-Cx (x = 7 and 11) Preparation

N,Ń-diundecyl-3,4,9,10-perylentetracarboxyldiimide (PTCDI-C11) was synthesized to corroborate its ability to enhance heterojunction cell performance. PTCDI-C11 was obtained by condensation of 3.24 mmol of 3,4,9,10-perylenetetracarboxylic di anhydride (PTCDA) with 5.57 mmol undecylamine and 0.19 mmol sulfuric acid. The mixture was heated to 100-120 °C and the obtained product was filtered and washed with methanol. To the precipitate, dilute NaOH solution was added and the mixture boiled. The residue was filtered off, washed with hot water and dried. This compound is sufficiently soluble in chloroform to allow chromatographic purification.

^{1}HNMR (200 MHz/$CDCl_3$): δ (ppm vs TMS) = 8.724 – 8.63 (m, 8H, from the perylene ring); 4.21 (t, 4H, from $N-CH_2-$); 1.78-1.41 (quin, 4H, from $N-CH_2-CH_2-$); 1.20 – 1.36 (m, 32H, from $-(CH_2)_8-CH_3$); 0,87 (t, 6H, from $-CH_3$).

FT-IR (KBr) 2953, 2927, 2849, 16975, 1657, 1593, 1508, 14667, 14389, 14045, 1379, 1343, 1299, 12467, 1091, 853, 809, 794, 747, 729 cm^{-1}.

$C_{46}H_{54}O_4N_2$ elemental analysis (weight %). Found: C: 79. 1; H: 10.0; N: 3.9. Calcd.: C: 79.1; H: 7.7, N: 4.0.

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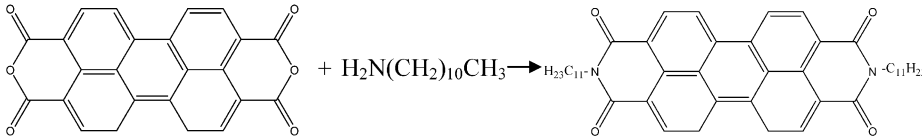


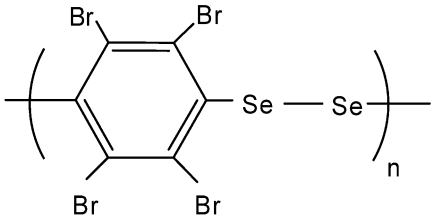
PTCDA PTCDI-C11

N,N′-diheptyl-3,4,9,10-perylentetracarboxyldiimide (PTCDI-C7)[10,11] was synthesized and characterized following the same above described procedure. This compound is sufficiently soluble in chloroform to allow a chromatographic method of purification. Yield: 85%. PTCDI-C7 HOMO/LUMO, –6,30 and –4,30 eV respectively, were estimated by electrochemical means demonstrating that the compound can be used as electron acceptor in a heterojunction with copper phthalocyanine.[11]

PTBrPDSe Preparation

Poly(tetrabromo-p-phenylenediselenide) (PTBrPDSe)[14] was previously synthesized and characterized by the authors at the Faculty of Chemistry of the Universidad Católica de Chile according to the following procedure. 2.35 mmol hexabromobenzene dissolved in 20 mL of pyridine was added to a sodium chalcogenide solution prepared in situ from 6.9 mmol of Na and 4.82 mmol of black Se in 10 mL. DMF. The mixture was refluxed for 30 min. and then precipitated in aqueous HCl with ice.

The precipitated polymer was filtered, washed and vacuum dried until constant weight.



PTBrPDSe

Solar Cell Preparation and Characterization

Before solar cells preparation the polymer was characterized by FT-IR spectroscopy, elemental analysis and X-ray photoelectron measurements (XPS), from which the proposed structure was corroborated.

The solar cells were prepared and checked at the Nantes University.[12] The TCO electrode was a layer of indium tin oxide (ITO) onto a glass substrate supplied by SOLEMS. Organic materials such as copper phthalocyanine (CuPc), aluminium tris(8-hydroxyquinoline)(Alq_3) and 2(4-biphenyl)-5-(4-tertbutylphenyl)1,3,4-oxadiazole(T-butyl) were purchased from Aldrich and used as received. Organic compounds were sublimed under 10^{-4} Pa vacuum. PTBrPDSe polymer decomposition starts at T> 523 K[15] and PTCDI-C7 and PTCDI-C11 decomposition temperature is above 613 K, therefore during their sublimation the crucible temperature was kept below these values.

The thin film deposition rate and thickness were estimated *in situ* on a quartz monitor. The deposition rate and final thickness was respectively 0.05 nm s^{-1}, 35 nm for CuPc, and 0.05 nm s^{-1}, 40 nm for PTCDI-C7 and PTCDI-C11 and 0.05 nm s^{-1} and 8 nm for Alq_3. The thickness was selected after optimization.

A solar cell scheme is as follows.

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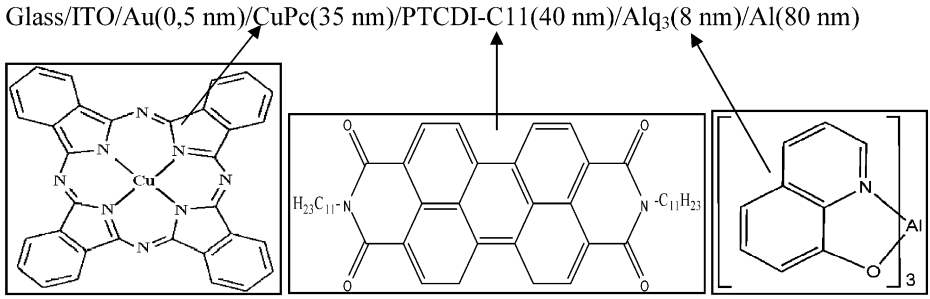
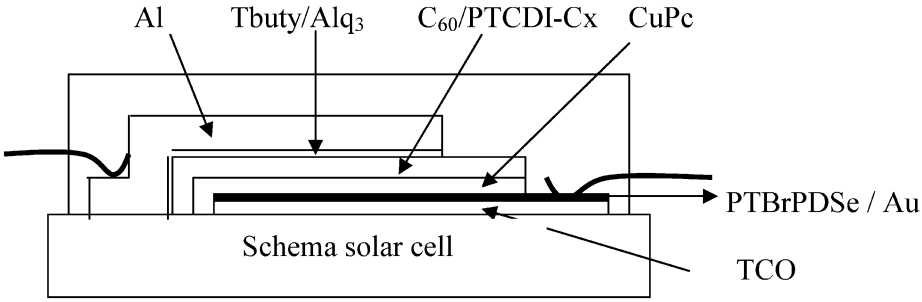


The organic film thickness was checked on a scanning electron microscope (SEM). After organic thin film deposition, aluminium upper electrodes was thermally evaporated (150 nm thick), without breaking the vacuum, through a 1.5 mm × 6 mm active area mask.

Electrical characterization was achieved on an automated I-V tester, in the dark and illuminated with 1 sun AM 1.5 Global simulated solar irradiation. Performance of photovoltaic cells was measured using a calibrated solar simulator (Oriel 300W) at 100 mW cm^{-2} light intensity adjusted with a



For PV-cells, organic materials were purified by vacuum sublimation. Besides, it was observed that using the same charge in the evaporation crucible led to "self-purification" of the product during the first depositions. Therefore, the results discussed herein correspond to cells deposited after at least five evaporation cycles of the organic products.

Bernède et al. showed that the presence of an ultra-thin metallic film at the TCO/organic material interface allows significant improvement in the power conversion efficiency of organic solar cells. Consequently, in most cases a very thin Au film (0.5 nm) was introduced at the ITO/CuPc interface.[12]

PV reference cell (0.5 cm^2 CIGS solar cell, calibrated at NREL, USA). Measurements were conducted under room conditions.

Results and Discussion

The power conversion efficiency of the cells prepared from these perylenes is similar, whatever the x value (see Figures 1 and 2). It was shown that PTCDI-C11 allows the open circuit voltage, Voc, of the cells to be increased but, at the same time, the short circuit current density, Jsc, decreases, which led us to conclude that the power energy conversion efficiency of both cell families is similar, which is in good agreement with the

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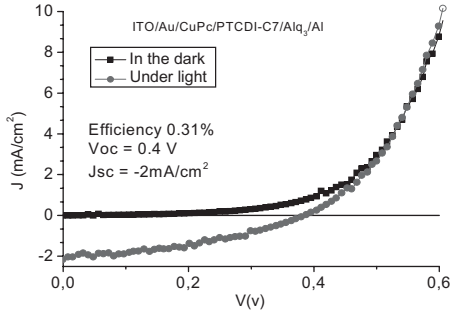

Figure 1.
J-V curves of a solar cell using PTCDI-C7 as acceptor layer. Glass/ITO/Au/CuPc/PTCDI-C7/Alq_3/Al.

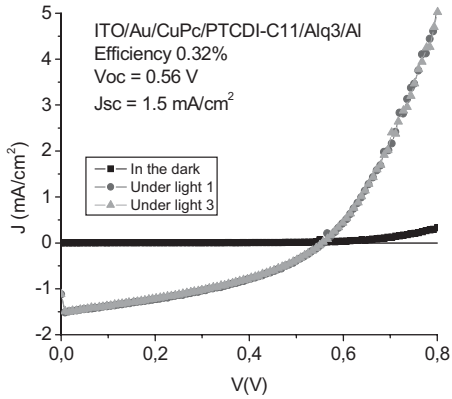

Figure 2.
J-V curves of a solar cell using PTCDI-C11 as acceptor layer. Glass/ITO/Au/CuPc/PTCDI-11/Alq_3/Al.

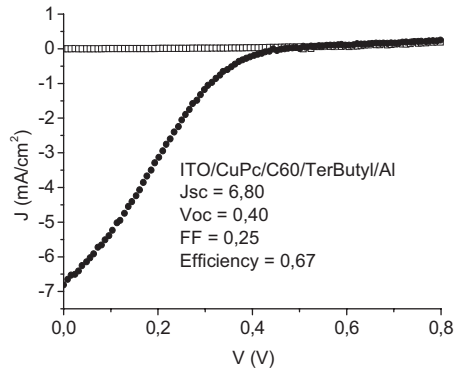

Figure 3.
J-V curves of a solar cell Glass/ITO/CuPc/C_{60}/Tbut/Al.

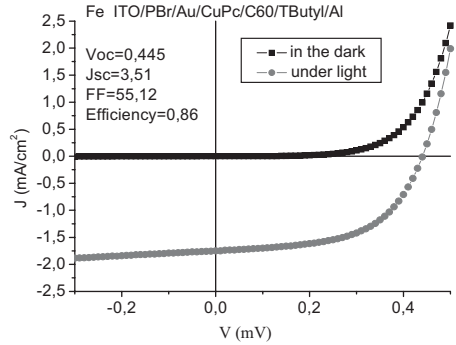

Figure 4.
J-V curves of a solar cell using PTBrPDSe as "buffer layer"Glass/ITO/PTBrPDSe/Au/CuPc/C_{60}/Tbut/Al.

fact that both acceptors belong to the same compound family.

In Figure 2, "light 1" means measure immediately after light illumination, "light 3" means measure after 10 minutes of light illumination.

The solar cell efficiency using CuPc/PTCDI-C11 junction is lower than that obtained with CuPc/C_{60} couple (see Figures 3 and 4). Moreover, the cell efficiency is improved when a buffer layer is introduced between anode and electron donor (see Figure 4). The slope at the short circuit point of the electrical cells characteristics is the inverse value of the shunt resistance (Rsh) of the equivalent circuit scheme of a solar cell. Indeed, a decrease of the open circuit voltage (Voc) and fill factor (FF) values can arise from pinholes, that short-circuit the PV cell and decreases the Rsh value. It can be seen from Figure 3 and Figure 4 that the buffer layer (see Figure 4) greatly decreases the slope at the short circuit point and therefore increases strongly the shunt resistance and the power conversion efficiency of the cells. The presence of the resistive PTBrPDSe thin layer (1 nm) prevents leakage effect of the diode. Indeed, lowering of Voc values can take place from pinholes, which short-circuit the PV cell and decrease the Rsh value. Successful interface modifiers should maximize Rsh through pinhole-free films formation.

In addition, it was demonstrated that the presence of a selenium-containing polymer

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chain in a polymer, *e.g.*, PTBrPDSe, can be tried as ''buffer layer'', improving thus photovoltaic cell efficiency. The challenge set to improve photocells efficiency leads us to develop new buffer layers.

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