

THE PHOTOVOLTAIC BEHAVIOR OF VACUUM DEPOSITED DIPHENYL-DIKETO-PYRROLOPYRROLE POLYMER

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Abstract. *Diphenyl-diketo-pyrrolopyrroles (DPP) are low molecular weight materials with promising luminescence and photovoltaic properties which are suitable for thin layer fabrication by a variety of methods like solution processed spin coating and physical vapour deposition (PVD). In this paper we investigate two types of Indium tin oxide (ITO)/Active material/Al structures: one with DPP derivative as active polymer layer with thicknesses of about 150nm and a second type of heterojunction solar cell based on DPP-C₆₀ composite films (ratio 60:40 mass %) with thicknesses of about 100nm. The samples in this study have been prepared by the means of PVD which has the capability to produce the whole multilayered structure in one vacuum cycle after which the samples were processed and encapsulated within inert atmosphere in a glove box. The surface morphology of the films was studied by Scanning Electron Microscope (SEM) imaging which revealed formations of grains with size of about 200-500nm in the DPP layers and spheres with size of about 100-200nm in the composite layer. The photovoltaic behavior was evaluated through the results of spectral sweep of the generated photocurrent and I-V characteristics in dark and under illumination with specific wavelength. The photovoltaic behavior was successfully demonstrated and directions toward performance improvements have been given.*

Key words: *photovoltaic behavior, diphenyl-diketo-pyrrolopyrrole, fullerene C₆₀, organic solar cells, physical vapour deposition*

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1. INTRODUCTION

Nowadays the organic solar cells (OSCs) are a subject of increased research and development efforts due to their flexibility and inexpensive processing. Their basic architecture is that of a sandwich type structure with stacked organic and inorganic thin films with high demands to their properties e.g., film homogeneity, thickness uniformity and roughness.

Diphenyl-diketo-pyrrolopyrroles (DPP) are low molecular weight materials with promising luminescence and photovoltaic properties [1] and [2]. The derivative, 1,4-diketo-3,6-diphenyl-pyrrolo-[3,4-c]-pyrrole (DPP) was first described in 1974. The reaction shown on Fig. 1 represents its first synthesis method, with synthesis yield from 5 to 20 % [3]. Later, different approaches for diketopyrrolopyrrole synthesis were found, for example synthesis from succinic acid diester using the strong base **Error! Reference source not found.** 1, 2], other methods are available in the literature as well **Error! Reference source not found.** 4].

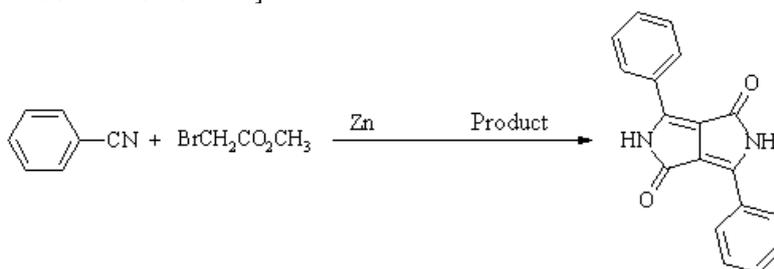


Fig. 1 Diketopyrrolopyrrole first synthesis.

DPP is very stable material, red in the solid phase, with very low solubility. Once dissolved, the obtained solution is yellow with a little bit of green. Absorption maximum between solid state and solution differs (cca 500 nm \rightarrow cca 540 nm) because hydrogen bonds are broken and π -electron overlaps and the crystal structure is cancelled.

In 1986, the first derivative was introduced to the market and since then, many other derivatives have been synthesized and are a subject of patents in many areas of application like organic field-effect transistors [5], OLED devices [6], solid-state dye lasers [7] and as a luminescent media in a polymer matrices [8].

Presently these compounds are object of intensive research because they exhibit a variety of shades in the solid state and especially chemical, light and thermal stability [9].

DPP itself has a high molar absorption coefficient, as well as high quantum yield of fluorescence, therefore low molecular weight derivatives of DPP and DPP based polymers have been extensively studied on their optical and photovoltaic properties [10–15] and have found their place in the organic electronics as a promising candidate for the future organic solar cells.

This paper deals with 3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl) pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione denoted hereafter as DPP. Using this material as donor for bulk heterojunction based solar cells leads to a photovoltaic conversion of efficiencies up to 4.4% [3].

To separate the strongly bound Frenkel excitons in organic films, the donor-acceptor concept was proposed [16]. So far, fullerene C₆₀ and C₇₀, as well their derivatives, are most successful acceptors for OSCs [17]. Power conversion efficiencies in the range of 6 ÷ 8% have been reported for solution-processed single junction bulk heterojunction solar cells combining fullerene derivatives as acceptor material and π -conjugated polymers as donors [18–21]. Conjugated system leads to the high charge carrier mobility across the structure. The thiophene rings secure the planarity of the molecule, so even adding the ethylhexyl solubilising groups does not break the conjugation.

Organic bulk-heterojunction solar cells comprising are reported to demonstrate lifetimes approaching seven years, which is the longest reported lifetime for polymer solar cells [22].

Small molecules show many advantages as higher possibility of supramolecular organization, higher purity and easier production [23]. They also do not suffer from batch to batch variations, broad molecular-weight distributions and end-group contamination [3]. Thin films of small molecular semiconductors are usually deposited by the means of complex fabrication methods such as chemical or physical vapour deposition, organic molecular beam epitaxy or solution-based deposition techniques (most notably spin coating). The performance of the resulting thin layers has been shown to be highly sensitive to film morphology and the processing conditions. Often, the solution processed active layers of the devices (e.g. spin cast films) exhibit a high portion of microcrystallites and aggregates whereas the vapour deposition techniques provide high quality crystalline films which are characterized by improved charge transportation [14]. Recently the relationship between the organic thin film morphology and the device performance is subject of intensive research.

We have chosen the DPP and its derivatives as the core material of our research because of its wide range of applications, proven photovoltaic properties and versatile thin film fabrication methods – thin films from this material could be made with solution processed methods like spin or spray coating and through vapour deposition processes like the PVD. We concentrated our efforts on the physical vapour deposition of DPP in order to obtain quality thin films which could be used as a reference for its performance and for future studies on its possible application as integrated optical detector.

Current paper consists of two main sections. In the *Experiment* section are presented the chemical structure of the used materials, fabrication process details (PVD parameters and process flow, encapsulation procedure, etc.), specification of the used equipment for fabrication and characterization of our test samples and their construction parameters (dimensions and arrangement). In the *Results* section are presented and analyzed images of the surface evaluation of the test samples with two complimentary methods – visual inspection with optical microscope under polarized light and SEM analysis. Further in this section are presented the results of the photovoltaic characterization and most notably spectral and *I-V* measurements of the samples.

2. EXPERIMENT

In the course of the present study two types of solar cell devices were prepared and evaluated. Their structure was [Glass substrate|ITO|*Active material*|Al|Encapsulation epoxy|Glass seal] where the “Active material” was either DPP polymer or the composite

thin film DPP-C₆₀ in a mass % ratio of 60:40. The chemical structure of the DPP polymer used in this study and the fullerene C₆₀ are presented on Fig.2.

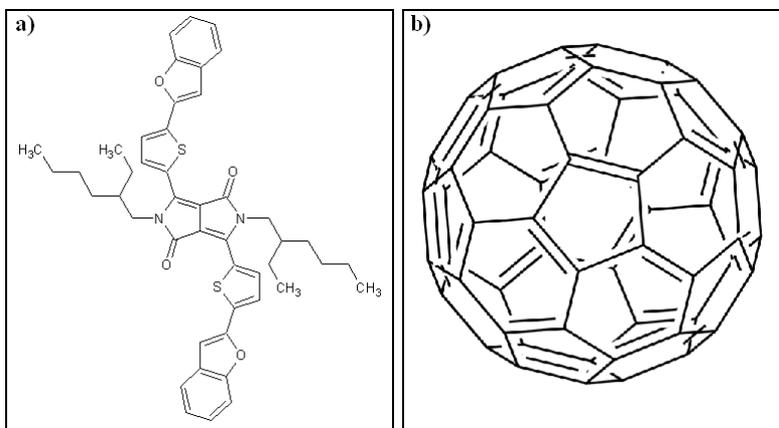


Fig. 2 Chemical structure of the DPP (a) and the fullerene C₆₀ (b).

The active material (DPP) was provided by Centre for Organic Chemistry Ltd. (COC), who synthesized it according to the route published in 2009 by Walker et al. [3]. Fullerene C₆₀ PCBM ([6, 6]-Phenyl-C₆₁-butyric acid methyl ester) was commercially purchased from Ossila Ltd.

For the fabrication of our samples we used “The Ossila OLED/OPV Pixelated Anode Substrate System” and “The Ossila Encapsulation System” consisting of: 20×15 mm sized pre-patterned ITO-covered glass substrates, active area and cathode deposition masks, encapsulation glass slides, encapsulation epoxy and electrical connection legs with standard 0.1 inch (2.54 mm) pitch.

The glass substrates had a specific ITO pattern which made it possible to obtain 6 solar cell samples on one substrate. The pattern was as follows: one cathode strip by the long side and three little strips (fingers) on both perpendicular sides, parallel to the cathode strip, which after deposition forms six active zones with dimensions 4×1.5 mm and the six anodes connected to them.

The active material thin film deposition was carried out in MBraun vacuum system at evaporation temperature of 180°C for the DPP and 420°C for the C₆₀ with rate of deposition accordingly 4.2 Å/s and 2.5 Å/s through the active area deposition mask. The thin film deposition was simultaneous from two sources for the composite type of samples. After deposition of the active layer, the samples were taken out in a glove box filled with nitrogen atmosphere, the mask was changed with the cathode deposition mask and they were returned back into the evaporation chamber. When the vacuum in the evaporation chamber has reached sufficient levels aluminum electrodes were deposited.

As a final and optional step the encapsulation procedure was carried out on some of the samples. The encapsulation procedure consists of covering the Al electrode area with encapsulation epoxy and on top of it an encapsulation glass and drying out the test sample under UV lamp for 30 minutes. The encapsulation procedure is performed again in the

glove box, without exposing the sample to oxygen. Selected samples were not encapsulated in order to be studied by Scanning Electron Microscope Philips 515.

A cross-section of the resulting fully fabricated and characterization-ready solar cell sample is given on Fig. 3.

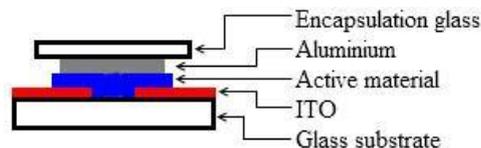


Fig. 3 Cross-section of the organic solar cell sample.

For the photovoltaic characterization we needed monochromatic light, which was produced by LOT-Oriel halogen lamp LSH502 and LOT-Oriel monochromator MSH101. The voltage applied was provided and the measurements of the generated photocurrent were carried out with Keithley 6517A electrometer and voltage source. And finally the light power was controlled and measured by the S120VC – Standard Si Photodiode Power Sensor and Keithley 485 picoammeter.

Photovoltaic measurements consisted of spectral dependence of the photocurrent at zero applied voltage; *I-V* characteristics, measured in both directions of the voltage scale in dark and exposed to monochromatic light.

All photovoltaic measurements were carried out on a vibration proof optical table from Standa.

3. RESULTS

3.1. Surface characterization

An optical microphotograph image of the prepared sample is presented on Fig. 4. As seen, uniform films entirely covering the ITO electrode area were obtained.

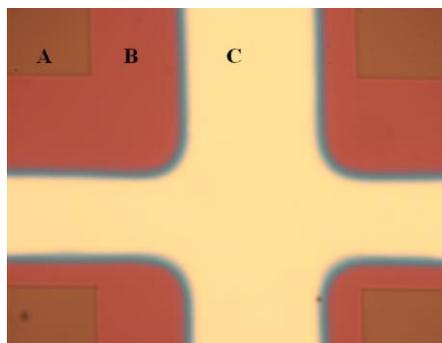


Fig. 4 The following device structure can be seen on the optical micrograph under polarized light: *A* – ITO electrode, *B* – active material and *C* – Al electrode.

The precise film surface characterization of the deposited pure polymer and composite active layers was performed by Scanning Electron Microscope (SEM). The SEM images taken at two different magnifications from the same sample without applying the encapsulation procedure are given on Fig. 5.

The images taken at the lower magnification of 20000 (Fig. 5a) for DPP films and magnification of 10000 (Fig. 5c) for the composite films of DPP-C₆₀ confirms that smooth and uniform thin films without a presence of pinholes were obtained.

The image taken at magnification of 40000 (Fig. 5b) of the DPP layer, reveals a formation of grains with size of about 200-500 nm. The observed grains follow a predominant orientation and could be related to a formation of crystallites, which is an expectable behavior of such low molecular weight compounds.

The SEM image taken at magnification of 40000 (Fig 5d) of the composite thin film, reveals a formation of spheres with a size of about 100-200 nm. The observed spheres could be related to a formation of single phase from one of the components.

To clarify these findings more investigation of samples with different DPP-C₆₀ ratio should be carried out and a comparison of DPP thin films deposited with other fabrication techniques should be performed.

In general it could be concluded that the deposited DPP polymer and DPP-C₆₀ composite films are suitable for electrical measurements in a “sandwich” type samples.

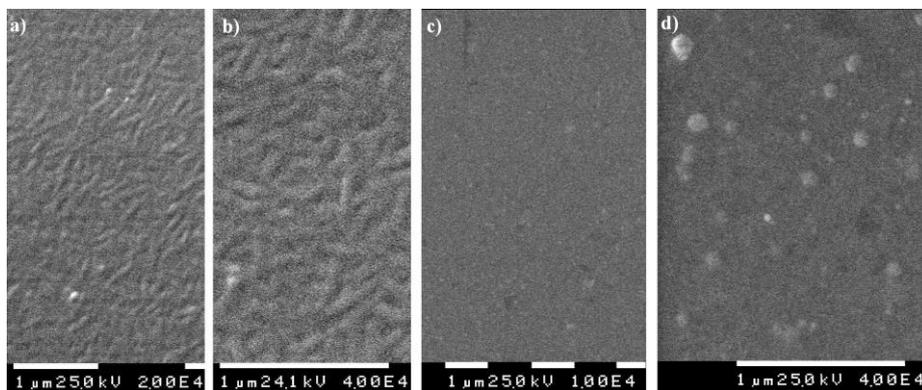


Fig. 5 SEM images of the deposited active layer thin films: a) DPP, magnification of 20000; b) DPP, magnification of 40000; c) DPP-C₆₀, magnification of 10000; d) DPP-C₆₀, magnification of 40000.

3.2. Photovoltaic characterization

Spectral dependences of the photocurrent, measured at zero applied voltage between the electrodes from ITO|Active material|Al structures are presented in Fig. 6. The solar cell samples with DPP thin films as active material exhibit a maximum of the spectrum at an excitation light wavelength of 400 nm (Fig. 6a). The stacked structures with composite thin films of DPP-C₆₀ as active material show a maximum of the spectrum at an excitation light wavelength of 533 nm (Fig. 6b).

Similar spectral dependences of the photocurrent taken from samples with the same materials as active layers, but prepared by spin-coating technique were published in the literature [3].

For an excitation of this peak during the next experiments a monochromatic light with wavelengths accordingly equal to the exhibited maximums were used.

As expected the addition of the fullerene C_{60} in the second type of solar cell samples under investigation has led to an increase of the generated photocurrent – around 15 times than the current generated by the pure DPP solar cell samples. Moreover there is a significant widening of the useful wavelength bandwidth – the heterojunction solar cell could be successfully utilized in the entire examined spectrum (from 350 nm to 800 nm) as opposed to the single polymer solar cell which is only useful in the range of 350 nm ÷ 500 nm.

Under illumination of monochromatic light the non-optimized samples produced photocurrent of almost two orders of magnitude higher than what was observed on the dark I - V measurements.

Processing the data for the structures, short circuit current J_{SC} and open circuit voltage U_{OC} were determined.

From the area confined by J_{SC} and U_{OC} , the dependences of the electrical power on the voltage applied are plotted on Fig. 8, right Y axis.

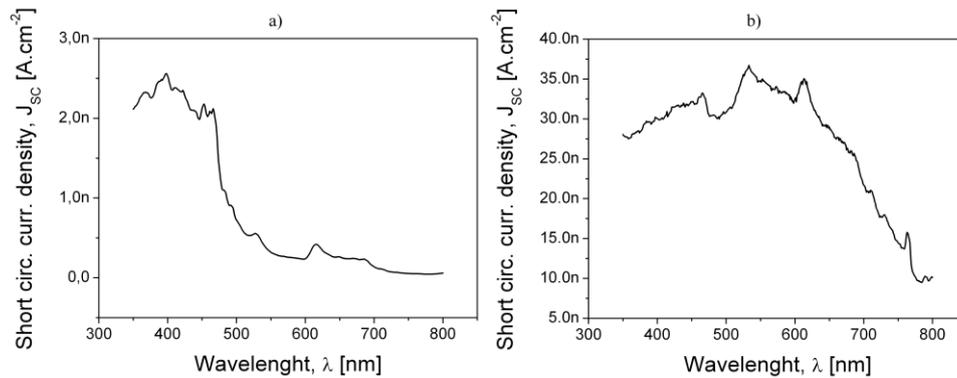


Fig. 6 Spectral dependence of the photocurrent at zero applied voltage:
 a) Single polymer, pure DPP solar cell ($\lambda_{max} = 400$ nm) b) Heterojunction solar cell, DPP- C_{60} composite with ration 60:40 mass % ($\lambda_{max} = 533$ nm).

The maximum electrical power P_{MAX} was found under the maximum power voltage U_{MP} and the maximum power short circuit current density – J_{MP} .

The results are given in Table 1.

Table 1 Photovoltaic parameters estimated from I - V curves.

Parameter	DPP	DPP- C_{60}	Dimension
J_{SC}	2,5	36	nA.cm ⁻²
U_{OC}	0,71	0,71	V

P_{MAX}	$8,4 \cdot 10^{-7}$	$12 \cdot 10^{-7}$	$\text{mW} \cdot \text{cm}^{-2}$
U_{MP}	0,5	0,25	V
J_{MP}	1,67	5,24	$\text{nA} \cdot \text{cm}^{-2}$

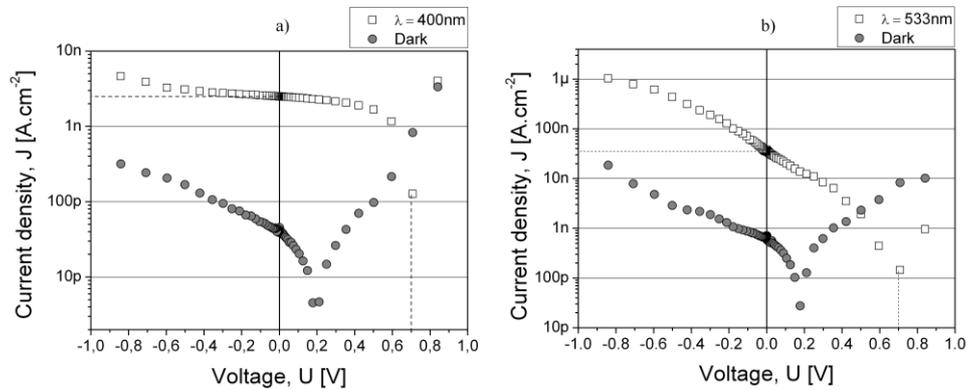


Fig. 7 *I-V* characteristics measured in the dark and under monochromatic light with irradiance of $0.95 \text{ mW} \cdot \text{cm}^{-2}$, a) DPP samples and b) DPP- C_{60} samples.

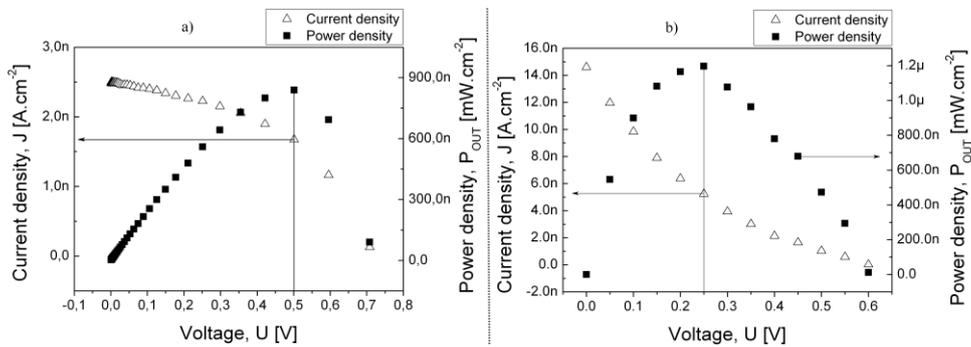


Fig. 8 Dependence of the power density (right Y axis) and current density (left Y axis) on the voltage applied, as calculated from and under the same conditions as Fig. 7, light curves, a) DPP samples and b) DPP- C_{60} samples.

4. CONCLUSION

Two types of ITO|Active material|Al structures were prepared by vacuum deposition and encapsulated in an inert atmosphere. The evaluated active thin layers were DPP with 150 nm thickness and a composite active layer with DPP and fullerene C_{60} simultaneously deposited from two evaporation sources, with thickness of 100 nm and mass % ratio of about 60:40.

The surface morphology of the fabricated thin films was studied by SEM imaging, which revealed formations of grains with size of about 200-500 nm in the DPP layers and spheres with size of about 100-200 nm in the composite layer.

Photovoltaic behavior was successfully demonstrated and evaluated. Although the basic construction of a single junction OSC showed expectedly low power efficiency, below 1%, it could be concluded that the vacuum deposited active layers have promising photovoltaic properties for incorporation in the future OSCs and other organic electronic devices. Further optimization should be made towards reducing the contact barrier and facilitating the excitation decay and charge carrier extraction through the addition of intermediate interface layers like Poly(3,4-ethylenedioxythiophene) Polystyrene sulfonate (PEDOT:PSS) and Ca. Other possible routes for optimizations include the thermal annealing of the newly formed thin layers [18], or optimization of the whole structure of the OSCs by introducing gold nanoparticles with different morphologies into buffer layers [24]; using more than one stacked photoactive layers with complementary absorption spectra to form multi-junction organic solar cells [25 – 27] or formation of radial electron contacts [28].

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