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# DEVELOPMENT OF PHOTOVOLTAIC DEVICES BASED ON ORGANIC/INORGANIC SEMICONDUCTORS

SPECIALITY 134.01 – MATERIALS PHYSICS AND TECHNOLOGY

**PhD in Physical Sciences thesis summary**

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The summary and PhD thesis can be consulted at the library of the Moldova State University and on the ANACEC website (*www.cnaa.md*).

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**SUMMARY**

## CONCEPTUAL RESEARCH MILESTONES

**Actuality and importance of the issue addressed in the paper:**

Organic compounds and supramolecular associations underpin new materials for photovoltaic energy. From the wide range of organic compounds, as combinations possessing excellent electric charge carrier donor molecules can be highlighted the unsubstituted metal phthalocyanines (MePc), as well as those modified / functionalized. Typically, phthalocyanine-based solar cells are produced by vapour deposition, despite the fact that solution deposition (for example spin-coating or drop-casting) is cheaper and offers more control over film structure. By deposition from solutions, different parameters (such as temperature, solvent, etc.) can affect self-organized structure formation in nucleation and growth processes during crystallization. The reason why the vapour deposition method is more commonly used lies in the low solubility of MePc in most solvents. Moreover, the processes of nucleation and growth of metal phthalocyanine aggregates in solutions are very complicated and not yet fully elucidated. To prepare MePc films from solutions, it is necessary to find the right solvents and optimize deposition techniques such as drop-casting (drop deposition on fixed substrate) and spin-coating (drop deposition on mobile substrate). There is a need to understand the processes of nucleation and growth, aggregation, precipitation, crystallization and to use this knowledge to produce the qualitative nanostructures on which the performance of organic semiconductor-based solar cells depends (OSSC).

Phthalocyanines make up a large group of synthetic substances, analogous to natural porphyrins, such as chlorophyll, blood heme and others. These combinations have attracted the particular attention of researchers for more than 90 years now. During this time, thousands of new phthalocyanine ligands and their complexes with metals in various oxidation states have been synthesized and identified, which are being intensively investigated in organic, physical and coordinative chemistry. Among other things, these combinations are proposed as molecular models for studying the behavior of natural porphyrins in various photophysical and photochemical processes. The high interest in phthalocyanines is explained by their many useful properties. It has already become traditional to use these combinations as photostable dyes and pigments [1] as well as catalysts in chemical, electrochemical and photochemical processes [2]. There are prospects for their use in electrophotography and jet printing, in photodiagnosis and therapy of oncological diseases [3], as materials for noxious gas detection sensors, etc.

As electron acceptor materials for obtaining double-layer, multilayer and bulk hetero-junction photovoltaic devices, the most commonly used are fullerene ($C_{60}$) and its functional derivatives, due to their high electronic affinity and the promising performance of the devices

produced. Fullerenes such as $PC_{71}BM$ are essential as electron acceptor material in the bulk heterojunctions of high-performance solar cells, but the given materials absorb visible light very poorly, reducing the volume of the fraction occupied by the high-absorbing donor material. Moreover, fullerenes have low tunneling capacity, restricting the development of conjugate systems for many attractive electronic structures to create higher voltages. Recent research has been carried out to replace these fullerenes with organic molecules that would contribute to better electron tunneling and light absorption. It has been found that, in addition to other candidates, perylene derivatives [4], which possess good chemical stability and high electron affinity, can serve as potential electron acceptor materials.

The great interest in phthalocyanines and perylene derivatives is confirmed by the publication of numerous scientific articles, textbooks, journals and monographs. Among the international monographs, the following works [5-7] and others deserve special mention. Questions related to the synthesis and research of phthalocyanines are discussed in detail in numerous editions of „The Porphyrin Handbook" [8] and in the specialized journal „Journal of Porphyrins and Phthalocyanines", published since 1997. The interest in basic and applied research on the given materials is mainly due to their potential application for the production and design of photovoltaic devices. Research into these materials is therefore fully justified by their promising physico-chemical properties for contributing to solving, at least in part, some of today's medical and energy problems.

In the given work, among the multitude of possibilities for the synthesis of photovoltaic devices, the synthesis method based on the processing of organic semiconductor materials from chemical solutions was selected and applied. The organic compound ZnPc (zinc phthalocyanine) was used as the basic semiconductor material for the production of Schottky-type devices. For the production of bulk heterojunctions, zinc phthalocyanine was used as electron donor and the functional perylene derivative - PTCDI was used as electron acceptor.

**Goal and objectives of the research:**

The main goal of this paper is to develop and optimize the technology for the synthesis of thin films based on zinc phthalocyanine from chemical solutions using the centrifugation method and the drop method, as well as to study the structural and optical properties of the obtained films for their implementation in the production of photovoltaic devices.

The following objectives have been set to achieve the proposed goal:

- Development of zinc phthalocyanine and PTCDI solubilization protocol;

- Optimization of the synthesis regimes of thin films of chemical solutions by the centrifugation method and the drop method, starting from the study of the morphology, structure and chemical composition of the synthesized films;
- Study the doping conditions of thin films in order to control their properties for photovoltaic applications;
- Investigation of correlations between microstructure and optical properties;
- Development of Schottky-type photovoltaic devices based on solution-processed zinc phthalocyanine films and study of their electrical and photoelectric properties;
- Development of bulk heterojunction photovoltaic devices based on mixed zinc phthalocyanine and PTCDI films; study of their electrical and photoelectric properties.

**Scientific problem solved:** Development of the synthesis technology of zinc phthalocyanine thin films by processing from chemical solutions and its optimization by investigating the electrical, photoelectric, optical, structural and morphological properties of Schottky diode and ZnPc bulk heterojunction ZnPc-based structures: PTCDI, for minimizing the production costs of organic solar cells prepared from chemical solutions, elucidating the physical principles of operation and finding solutions for increasing solar energy conversion efficiency.

**Main scientific results submitted for support:**

- The impact of the protic solvent FA on ZnPc molecules consists in the donor-acceptor mechanism of hydrogen cations, formed as a result of formic acid dissociation, to the nitrogen bridge atoms of the zinc phthalocyanine molecule and the adsorption of formate anions to the central zinc atom, resulting in the formation of ZnPc-formate complexes.
- *In situ* doping of zinc phthalocyanine with iodine involves the interaction of ZnPc and $I_2$ molecules with the protic solvent FA, resulting in the formation of $I^-$ and $I_3^-$ anions which, together with iodine molecules, hydrogen cations and formate anions, participate in the structural rearrangement and complexation of zinc phthalocyanine in the processed films. The formation of $ZnPc(HCOO^-)_x$, $ZnPc(HCOO^-)_xI_y$ and $ZnPcI_x$ complexes contributes to the broadening of the ZnPc band gap from 1.39 eV to 1.65eV and 1.85 eV.
- Heat treatment of thin films with ZnPc/FA, ZnPc:$I_2$/FA and mixed ZnPc:PTCDI/FA, ZnPc:PTCDI:$I_2$/FA compositions contributes to the improvement of their surface morphology by reducing surface roughness and increasing the size of nanogranules (~0.3 μm → ~0.9 μm), the process being accompanied by the removal of molecular iodine at temperatures above 100 $^oC$, the removal of the PTCDI perylene component with the

transition of ZnPc to the stable β phase in the temperature range 200-300 $^{o}$C and the desorption of formate ions at temperatures above 300 $^{o}$C.

- ZnPc-formate complex formation and iodine doping provides improved absorbance of processed thin films from solutions by broadening and shifting the solvatochromic B and Q bands of zinc phthalocyanine to longer wavelengths ($\Delta_{\lambda}B \sim 100$ nm, $\Delta_{\lambda}Q \sim 120$ nm), allowing these films to be used to fabricate Schottky-type devices with higher conversion efficiencies than those obtained from films deposited by thermal vacuum evaporation.
- High milliampere/cm$^2$ values of short-circuit current density for photovoltaic devices based on bulk heterojunctions with ITO/PEDOT:PSS/ ZnPc:PTCDI/Al and ITO/PEDOT: PSS/ZnPc:I2:PTCDI/Al structures is due to electron transfer from the ZnPc$(HCOOH)_x$ and ZnPc$(HCOOH)_xI_y$ complexes, acting as electron donors, to the PTCDI acceptor component during light penetration and absorption in the semiconductor layer of the photovoltaic device.

**Approval of scientific results:**

The scientific results obtained have been reported and discussed at the following national/international conferences:

- 8$^{th}$ and 9$^{th}$ International Conference MSCMP, Chisinau, Republic of Moldova, 2016 and 2018;
- International Student Innovation and Scientific Research Exhibition *„Cadet INOVA '17"* and *„Cadet INOVA '15"* Sibiu, Romania, 2017 and 2018;
- International Exhibition of Inventions and Innovations „Traian Vuia 2017", Timisoara, Romania, 2017;
- International Salon of Research, Innovation and Technological Transfer „Inventica 2017" and „Inventica 2018", Iasi, Romania, 2017 and 2018;
- Le cinquième colloque francophone PLUridisciplinaire sur les Matériaux, l'Environnement et l'Electronique (PLUMEE 2017), Bacau, Romania, 2017;
- International Specialized Exhibition „Infoinvent 2017" and „Infoinvent 2019" Chisinau, Republic of Moldova, 2017 and 2019;
- National Scientific Conference with International Participation „Integration through Research and Innovation", Chisinau, Republic of Moldova, 2017 and 2018;
- 38$^{th}$ Research World International Conference, Tokyo, Japan, 2017;
- International Fair of Innovation and Creative Education for Youth „ICE-USV", IInd and IVth edition, Suceava, Romania, 2018 and 2020;
- European Exhibition of Creativity and Innovation „EuroInvent", Iasi, Romania, 2019;

- 3rd International Conference on Applied Surface Science „ICASS 2019", Pisa, Italy, 2019;
- Exhibition of Scientific Research, Innovation and Invention „PRO INVENT", XVIIIth edition, Cluj-Napoca, Romania, 2020;
- The I$^{st}$ International Exhibition „InventCor", December 17 - 19, Deva, Romania, 2020.

**Scientific results** presented at national and international exhibitions were appreciated with:

- 10 gold medals
- 2 silver medals
- An ELITE INNOVATOR award

and are authenticated by two **patents of invention**:

1. **FURTUNA, Vadim**, DUCA, Dumitru, POTLOG, Tamara. *Process for obtaining ZnPc-based Schottky diode.* Patent of invention 4535 (13) C1, H01L 29/872 (2006.01); H01L 21/04 (2006.01); H01L 31/0236 (2006.01). Moldova State University. Deposit Number A 2016 0129. Date of deposit 24.11.2016. Published 30.11.2017. In BOPI number 11, 2017, p.32
2. **FURTUNA, Vadim**, POTLOG, Tamara. *Process for obtaining zinc phthalocyanine-based volume heterojunction.* Patent of invention 4638 (13) C1, H01L 21/04 (2006.01); H01L 21/18 (2006.01); H01L 21/20 (2006.01); H01L 31/0236 (2006.01); H01L 21/04 (2006.01). Moldova State University. Deposit Number A 2018 0010. Date of deposit 19.02.2018. Published 30.06.2019. In BOPI number 6, 2019, pp. 46-47.

**Publications on the thesis topic:** The main results, obtained during the scientific research on the PhD (doctoral) thesis, were published in 30 scientific papers: 7 articles (2 of which in international journals with impact factor) and 23 abstracts at international scientific conferences. (The list of publications is attached at the end of the given abstract of the thesis).

**Volume and structure of the thesis:** The thesis consists of an introduction, 5 chapters, conclusions, recommendations and bibliography. It contains 196 pages, including 146 pages of basic text, 93 figures, 16 tables, 4 appendices (with 6 figures and 2 formulae) and a bibliography with 243 titles.

**Keywords:** Zinc phthalocyanine, formic acid, PTCDI, iodine, bulk heterojunction, Schottky-type structure, solar cell, interface, solar energy conversion, photovoltaic parameters

## THESIS CONTENT

The **Introduction** argues the actuality of the research topic, formulates the goal and objectives of the paper, the novelty and scientific originality of the paper, the scientific problem solved, the theoretical significance and applicative value, the main scientific results submitted for

support, the approval of the scientific results and the publications on the topic of the thesis, as well as the summary of each chapter of the thesis.

The first part of **Chapter 1** contains a detailed description of the structures and properties of metallophthalocyanines and the main methods for their synthesis from various precursors. Section 1.2 of the chapter describes current challenges and recent advances in the field of organic photovoltaics, and section 1.3 describes in detail and critically analyses, from a scientific and economic perspective, the technologies for obtaining thin films. The advantages and disadvantages of different thin film deposition methods are presented and arguments are made in favor of the application of technologies based on the processing of films from chemical solutions. Particular attention is paid to the problem of iodine doping of ZnPc films in photovoltaic devices [9] and to the dependence of photovoltaic device parameters on the cathode material [10, 11]

In the last section of the chapter, aimed at the selection of suitable solvents for the synthesis of zinc phthalocyanine thin films by solution processing, a review of existing literature data [12] on the solubility of unsubstituted metallophthalocyanines in different solvents is presented.

**Chapter 2** contains personal contributions made in the synthesis of zinc phthalocyanine and obtaining thin films based on it. It describes the method for the synthesis of ZnPc using phthalonitrile as a precursor. The systematic study of the solubility of ZnPc in the solvents chosen for the research is presented and the considerations underlying the selection of formic acid (FA) as the main solvent are described.

The concentrations of the saturated solutions and the values of the molar extinction coefficient were determined from spectroscopic measurements, using the Beer-Lambert law, which expresses the relationship between the absorbance, $A_\lambda$, the concentration of the solution, $c$, the molar extinction coefficient, $\varepsilon_\lambda$, for absorbing species at wavelength $\lambda$ and the distance travelled by the light,

$$A_\lambda = \varepsilon_\lambda c l \quad (1)$$

To determine the concentration of the saturated ZnPc/FA solution, the data corresponding to the solvatochromic absorption band Q for three solutions of known concentration were used to construct the calibration curve (Figure 1 b). To ensure linearity of absorbance dependence on concentration in the calibration curve, the saturated ZnPc/FA solution obtained from the solubility protocol was diluted 400-fold. The absorbance spectrum (Figure 1a) obtained for this solution confirms the splitting of the solvatochromic band Q.

Subsequently, the equation of the line for the calibration curve was also constructed using the absorption spectrum data for three ZnPc/FA solutions of known concentration at wavelength 718 nm, where the absorption maximum was recorded (Figure 1b).

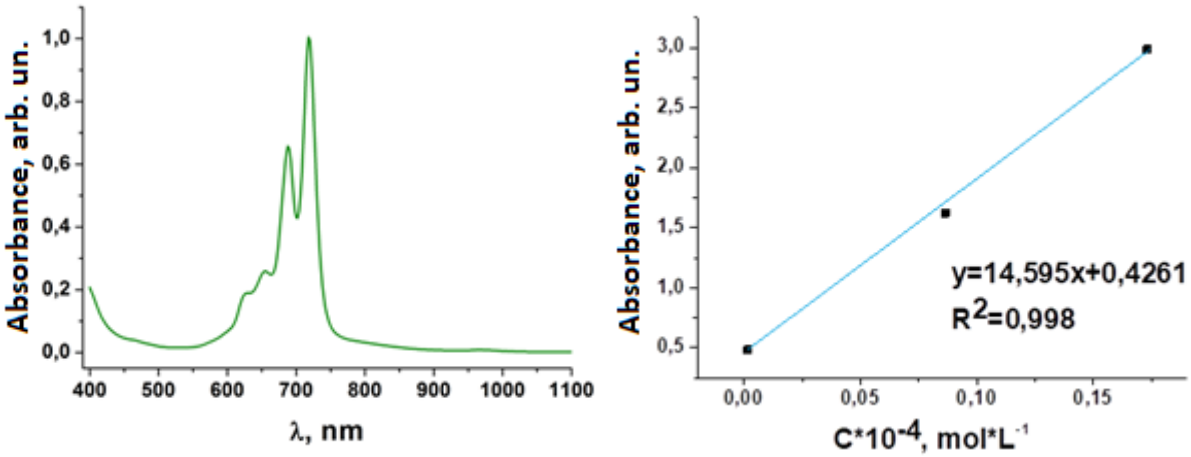



Figure 1. Absorption spectrum of ZnPc/FA for saturated solution, diluted 400-fold (left) and calibration curve (right).

For the solution of unknown concentration, which was obtained by 400-fold dilution of the saturated solution, an intensity value of 2,002 was recorded for absorbance. Thus, using the equation obtained for the calibration curve (Figure 1b), the molar concentration value was calculated for the given solution: $C_{M'}(ZnPc) = 0{,}108 \cdot 10^{-4} mol \cdot L^{-1}$ and for the saturated ZnPc/FA solution, respectively: $C_M(ZnPc) = 43{,}2 \cdot 10^{-4} mol \cdot L^{-1} = 4{,}32 mol \cdot m^{-3}$, with an average relative error of about 2%. The main sources of systematic errors that generated this value of the average relative error are: 1) Instrumental error of the JA-1003C analytical balance with which the mass measurements for ZnPc were performed and 2) Errors in the measurement of the volumes of solvent FA, used for preparation of the saturated solution, as well as those used for repeated dilutions of the solutions.

The molar extinction coefficient was determined by applying to equation (1) the concrete values for: the molar concentration of the solution obtained by diluting the saturated ZnPc/FA solution a 400-fold and the width of the cuvette.

$$A_\lambda = \varepsilon_\lambda c l \tag{2}$$

$$\varepsilon_\lambda = \frac{A_\lambda}{cl} = \frac{2{,}002}{0{,}108 \cdot 10^{-4} mol \cdot l^{-1} \times 1 cm} = 1{,}85 \cdot 10^5 L \cdot mol^{-1} \cdot cm^{-1}$$

The obtained value is in good agreement with the data given in the literature. This high value of the molar extinction coefficient confirms the very good absorption of light on the spectral range corresponding to the solvatochromic band Q by the saturated ZnPc/FA solution and encourages the use of this type of solution in the processing of ZnPc semiconductor thin films for the development of photovoltaic devices.

To clarify the nucleation and growth processes in the films deposited by the centrifugation method, experimentally seven solutions of different concentrations were prepared by diluting concrete aliquots from the saturated ZnPc/FA solution (Figure 2).

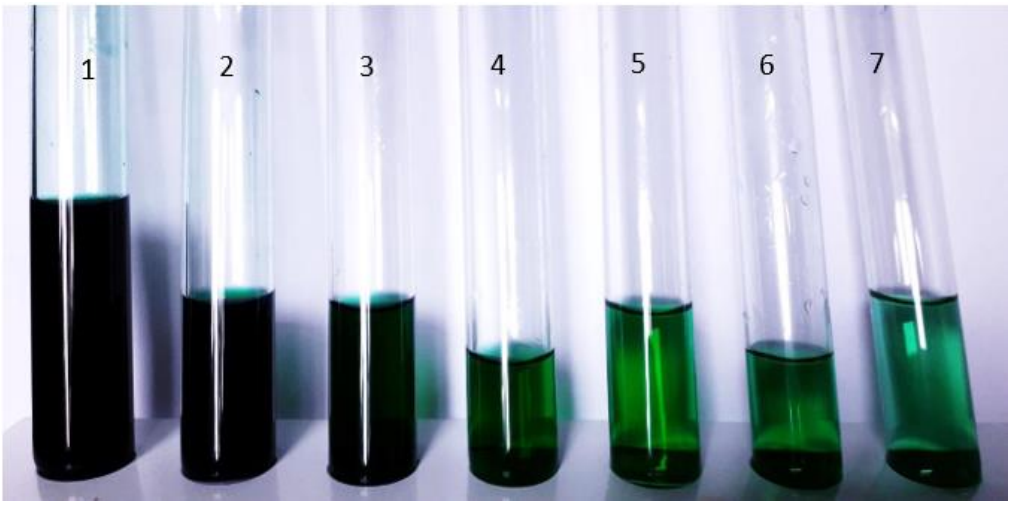



Figure 2. Solutions 1-7 of ZnPc/FA, with concentrations 4,32 - 0,0432 mol·m$^{-3}$.

The values of the concentrations of these solutions as well as the amounts of ZnPc deposited on the substrate (Γ) (coverage) [13] are shown in Table 1.

Table 1. Concentrations of solutions deposited by centrifugation and Γ values.

| № | Molar concentration of the solution, *mol·m$^{-3}$* | Γ, *10$^{-6}$mol·m$^{-2}$* |
|---|---|---|
| 1 | 4.32 | 28.944 |
| 2 | 2.16 | 14.472 |
| 3 | 1.08 | 7.236 |
| 4 | 0.432 | 2.894 |
| 5 | 0.216 | 1.447 |
| 6 | 0.0864 | 0.578 |
| 7 | 0.0432 | 0.289 |

The values for Γ were calculated based on the formula:

$$\Gamma = \frac{N(h \longrightarrow 0)}{A} = h_0 c_0 \approx 6.7 \times 10^{-6}[m] c_0, \quad (3)$$

where $c_0$ is the molar concentration of the ZnPc/FA solution used for centrifugation and $h_0$ is the thickness of the processed film at the time of transition.

For morphological and structural characterization, a set of thin films were prepared and processed according to the data in Table 2.

Table 2. Films obtained by the drop casting method

| Film number | Method of obtaining the film | | |
|---|---|---|---|
| | Composition of the solution | Number of solution volumes deposited on the substrate, ml | Thin film treatment temperature, $^{o}$C |
| 1A | Saturated ZnPc/FA solution | 2 | 20 |
| 1B | Saturated ZnPc/FA solution | 2 | 100 |
| 1C | Saturated ZnPc/FA solution | 2 | 200 |
| 1D | Saturated ZnPc/FA solution | 2 | 300 |
| 1E | Saturated ZnPc/FA solution | 2 | 400 |
| 1F | Saturated ZnPc/FA solution | 1 | 20 |
| 1G | Saturated ZnPc/FA solution | 3 | 20 |
| 1H | Saturated ZnPc/FA solution | 4 | 20 |
| 2A | ZnPc/FA + $I_2$/FA, 4:1* | 2 | 20 |
| 2B | ZnPc/FA + $I_2$/FA, 4:1 | 2 | 100 |
| 2C | ZnPc/FA + $I_2$/FA, 4:1 | 2 | 200 |
| 2D | ZnPc/FA + $I_2$/FA, 4:1 | 2 | 300 |
| 2E | ZnPc/FA + $I_2$/FA, 4:1 | 2 | 400 |
| 3A | ZnPc/FA+ PTCDI/FA, 4:1 | 2 | 20 |
| 3B | ZnPc/FA+ PTCDI/FA, 4:1 | 2 | 100 |
| 3C | ZnPc/FA+ PTCDI/FA, 4:1 | 2 | 200 |
| 3D | ZnPc/FA+ PTCDI/FA, 4:1 | 2 | 300 |
| 3E | ZnPc/FA+ PTCDI/FA, 4:1 | 2 | 400 |
| 3F | ZnPc/FA+ PTCDI/FA, 1:4 | 2 | 200 |
| 3G | ZnPc/FA+ PTCDI/FA, 2:3 | 2 | 200 |
| 3H | ZnPc/FA+ PTCDI/FA, 3:2 | 2 | 200 |
| 4A | ZnPc/FA+ PTCDI/FA+$I_2$/FA, 4:1:1 | 2 | 20 |
| 4B | ZnPc/FA+ PTCDI/FA+$I_2$/FA, 4:1:1 | 2 | 100 |
| 4C | ZnPc/FA+ PTCDI/FA+$I_2$/FA, 4:1:1 | 2 | 200 |
| 4D | ZnPc/FA+ PTCDI/FA+$I_2$/FA, 4:1:1 | 2 | 300 |
| 4E | ZnPc/FA+ PTCDI/FA+$I_2$/FA, 4:1:1 | 2 | 400 |

*- the figures indicate the molar ratio of the components: ZnPc, PTCDI, $I_2$

In the final section of the chapter, the investigation techniques used to characterize the properties of the materials and devices studied are briefly presented. The main analytical methods used to investigate surface topography and roughness, morphology, composition and structure of samples are reviewed, such as Atomic Force Microscopy - AFM, Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDX), X-ray Diffraction - XRD. Fourier Transform Infrared Spectroscopy (FTIR) was used to highlight the main functional groups in the molecular structure of the materials. Vibrational Raman spectroscopy is a complementary method to FT-IR spectroscopy and has been used to study the molecular vibrations of chemical bonds present in samples. Elemental analysis, identification of the atomic species present in the sample, chemical composition of the surfaces of the materials obtained and identification of their oxidation states was studied with X-ray photoelectron spectroscopy (XPS). The absorbance spectra of the samples were measured in the wavelength range 200-1100 nm with UV-VIS spectrophotometry and the changes produced in the molecules as a result of electronic transitions

induced by radiation in the ultraviolet and visible range were studied. To study the characteristics of the devices, current-voltage characteristics in the dark and illumination were studied with Keithley voltage source model 4200-SCS and solar simulator. External quantum efficiency characterization system includes light source (100W Xenon lamp), monochromator (wavelength range 350-1100 nm, spectral bandwidth 5 nm), detector, „beam chopper" controller with amplifier, specific software and calibration cell.

The initial sections of **Chapter 3** include morphological and structural characterization of processed thin films of pure ZnPc, $I_2$-doped ZnPc and ZnPc:PTCDI. The surface morphology of thin films deposited by centrifugation on different substrates was analyzed using atomic force microscopy (AFM). The images in Figure 3 show the nanogranules in the films obtained by centrifuging 1 ml of ZnPc/FA solution of different concentrations on a glass substrate. Figure 3 (1) shows the AFM image for glass, on a 5x5 $\mu m^2$ surface, and (2) - (6) - the AFM images, on the same 5x5 μm2 surface, for thin films obtained from ZnPc/FA solutions of the concentrations indicated on the corresponding images.

It should be noted that, for each individual case, the volume of 1 ml ZnPc/FA solution was deposited by the centrifugation method, dropping the solution successively at time intervals of approximately 2 s.

1) The glass surface, unlike that of $SiO_2$, is embossed, with the distance between its „highs" and „lows" varying within 10 nm.
2) For the lowest amount of material per unit area of 0.28944 $\mu mol \cdot m^{-2}$ (for the ZnPc solution of the lowest concentration), the formation of small, rarefied aggregates (clusters, nanogranules) with diameters around 80 nm is observed. It is remarkable that when the solution of the same concentration is successively dripped onto the substrate, the number of nanogranules does not increase, but their height increases slightly, up to ~ 95 nm.
3) For twice the amount of material per unit area we observe an increase in the number of aggregates, as well as a doubling of their planar dimensions, their height remaining approximately the same.
4) For the amount of material of 2.8944 $\mu mol \cdot m^{-2}$ we observe a significant increase in the number of aggregates as well as in their spatial dimensions. We note the presence of smaller-sized nanogranules (with an average diameter of about 80 nm) among those with larger spatial dimensions (whose average diameter is about 250 nm), for which, on the other hand, we observe a tendency to limit the three-dimensional growth.

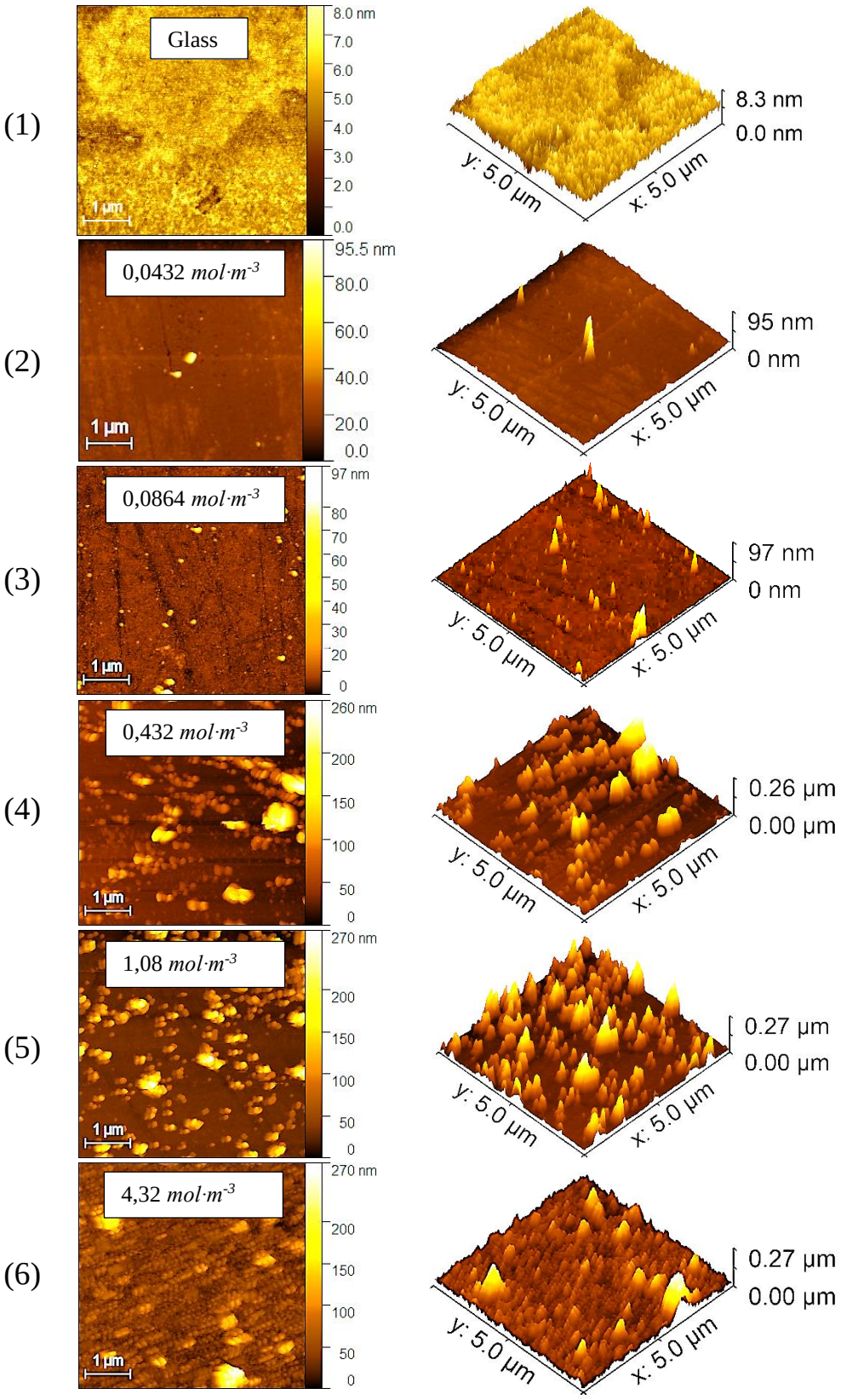



Figure 3. AFM images of ZnPc films deposited by centrifugation from ZnPc/FA solutions of different concentrations.

5) For the film obtained by processing the 1.08 μmol·m$^{-3}$ solution, at the amount of material per unit area of 7.236 μmol·m$^{-2}$ the number of nanogranules continues to increase, significantly reducing the distance between them. We observe the tendency for aggregates to associate and grow to approximately the same height (270 nm) and planar size (250nm x 250nm).
6) For the film obtained by processing the saturated ZnPc/FA solution, we observe the interconnection between the nanogranules in the film, their height tending towards the same limit (270 nm).

The study of the morphology of the films deposited by the drop method was carried out using scanning electron microscopy (SEM).

Based on AFM and SEM images, the processes of formation and growth of nanogranules in the deposited films are described, considering the cooperative mechanism of interaction between the species present in the solutions used and the substrate.

This chapter also includes the structural characterization of the processed films by identifying and indexing diffraction maxima from the diffractograms recorded by X-ray diffraction. From the recorded XRD diffractograms, the average crystallite size was determined using the Scherrer formula. XRD structural analysis revealed the impact of FA solvent on the resulting ZnPc molecules with the formation of ZnPc-formed complexes. Iodine doping contributes to the structural rearrangement and formation of $ZnPcI_x$, $ZnPc(HCOO^-)_xI_y$ complexes. Also shown are the diffractograms recorded for samples that have been heat treated. In the temperature range 200 - 300 $^oC$ the transition of ZnPc to the stable β phase and the removal of PTCDI from the iodine undoped thin films occurs. Chemical analysis of the thin films using X-ray photoelectron spectroscopy (XPS) confirmed the presence of the triiodide ion $I_3^-$ in the synthesized thin films and the connection of iodine with zinc in the ZnPc molecule (signal at 619, 8 eV), thus authenticating the proposed interaction mechanisms for particles present in dispersed systems. In order to verify and confirm the interaction mechanisms between the particles present in the synthesis solutions and to characterize the composition and chemical-structural properties of the synthesized thin films, FTIR spectra analysis on the 400 - 2000 cm$^{-1}$ range was performed for all synthesized samples. FTIR analysis confirmed the binding of hydrogen cations, formed during FA dissociation, to non-pyrrolic nitrogen atoms in the ZnPc molecule and desorption of formate ions from the central zinc ion at temperatures above 300 $^oC$. The FTIR data obtained for the films made it possible to interpret at a qualitative level the main structural changes, but also to point out some fine details highlighting the degree of ordering, i.e. the change in the ratio of crystallinity indices

within these types of materials. The presence of iodine species in the doped thin films was also confirmed by Raman analysis at the wavelength of 532 nm excitation light.

As a result of the structural analysis, the most likely mechanism of interaction of ZnPc with formic acid (FA) was determined, shown in Figure 4.

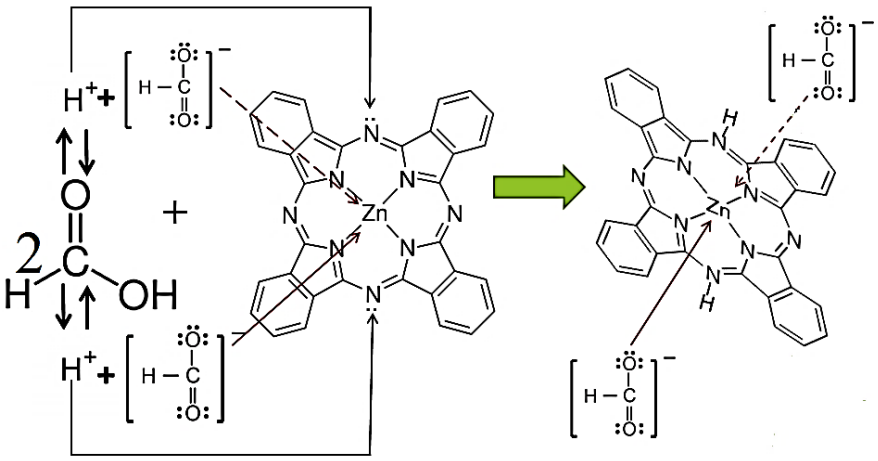
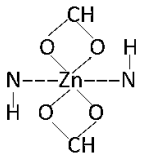


Figure 4. Mechanism of interaction of ZnPc molecules with solvent (FA)

The protic solvent FA, being a monobasic acid, partially dissociates in a single step with formation of hydrogen cations and formate anions. During particle diffusion through the dispersion system and during the evaporative phase-out of non-dissociated formic acid molecules, formate ions migrate to the central zinc ion in the ZnPc molecule, being adsorbed by it, and $H^+$ ions, in turn, migrate to the nitrogen bridge atoms. These nitrogen atoms each have a pair of non-coupled electrons and serve as electron donors in the formation of the donor-acceptor covalent bond with hydrogen protons. Due to the size of the coordination sphere and the maximum coordination number for the central zinc ion, a maximum of 2 formate ions can be attached to it according to the scheme:



The structural changes that occur as a result of iodine doping are due to a new interaction mechanism involving iodine molecules and ions, along with the other components / particles present in the dispersed system. According to publications [14, 15], the interaction of MePc with iodine leads to the formation of new molecular complexes as shown in the equation:

$$ZnPc + (x/2)I_2 \rightleftarrows ZnPc(I)_x$$

and, according to the results of the paper [16], upon dissolution of $I_2$ in FA, the following processes most likely occur:

1. $HCOOH \rightleftarrows H^+ + HCOO^-$

2. $I_2 + HCOO^- \rightarrow HCOOI_2^-$ (slow process)

3. The given complex then rapidly decomposes according to the equation:

$HCOOI_2^- \rightarrow HCOOI + I^-$

4. $I^- + I_2 \rightleftarrows I_3^-$

On the other hand, according to the data in the publication [17], formic acid can react with iodine according to the equation:

$$HCOOH + I_2 = 2HI + CO_2$$

Based on these data presented in the literature and data revealed from XRD diffractograms, FTIR and Raman spectra, the interaction mechanism shown in Figure 5 has been established. $H^+$ cations resulting from the electrolytic dissociation of FA and the small amount of HI (obtained from the interaction of FA with $I_2$) migrate to the nonpyrrolic nitrogen atoms and bind to them by covalent bonding with donor-acceptor mechanism. Some of the iodide $I^-$ ions migrate to the ZnPc-formed complex (most likely to the central Zn atom, but it is also possible that the migration is directed to those nitrogen-bridge atoms that have been protonated), and some interact reversibly with the iodine molecules to form triiodide ions. The brown color of the $I_2$/FA solution confirms the presence of $I_2$ molecules in the system. During the evaporation of FA molecules from the solution, the distance between ZnPc molecules decreases and the probability of their interconnection with iodine molecules via halogen bonds increases.

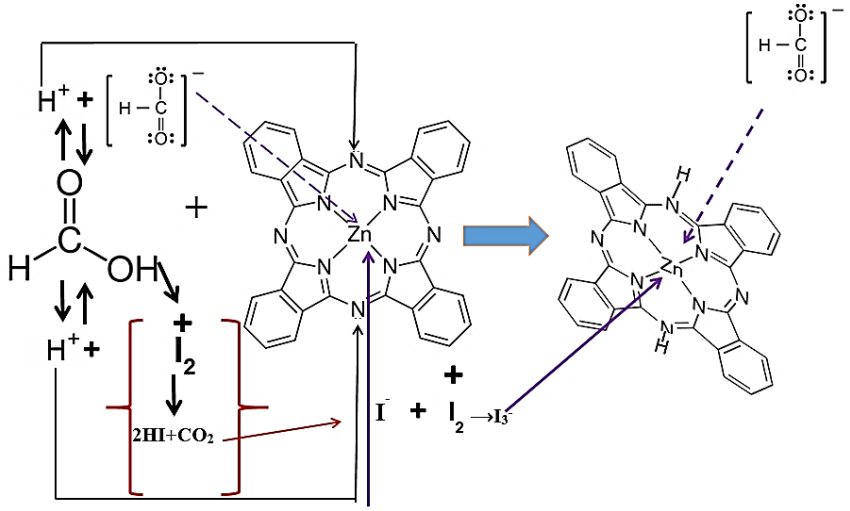



Figure 5. Scheme of interaction between ZnPc and FA with iodine.

From the spatial data within the system, it can be assumed that ZnPc interconnects with the $I_2$ molecules in the plane (Figure 6) and the iodide ion is positioned between the planes. According to the above diffractogram data, the interplanar distance in the ZnPc films is about 1,2 nm, and the diameter of the $I^-$ ion is 220 pm, so it can lie freely between planes.

The chapter also contains absorbance spectra of ZnPc, $I_2$-doped ZnPc and ZnPc:PTCDI films. The UV spectra of the realized films generally show two broad energy bands and an increase

in absorbance of thin ZnPc films with increasing thickness. A shift of the absorption threshold towards longer wavelengths is observed for samples with larger thicknesses. This shift indicates a decrease in the forbidden energy band ($E_g$).

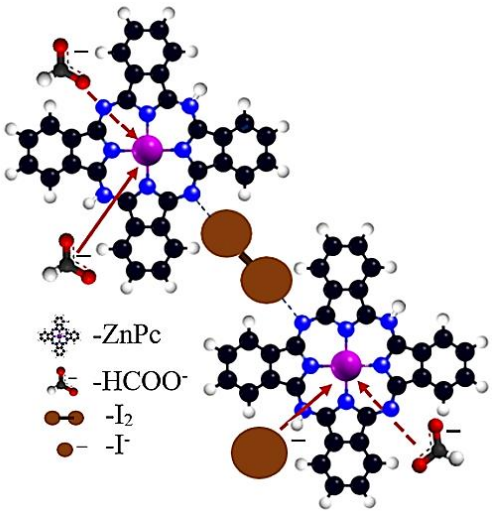



Figure 6. Interaction and interconnection of ZnPc molecules with iodine molecules via halogen bonds and migration of formate and iodide ions towards the central zinc ion.

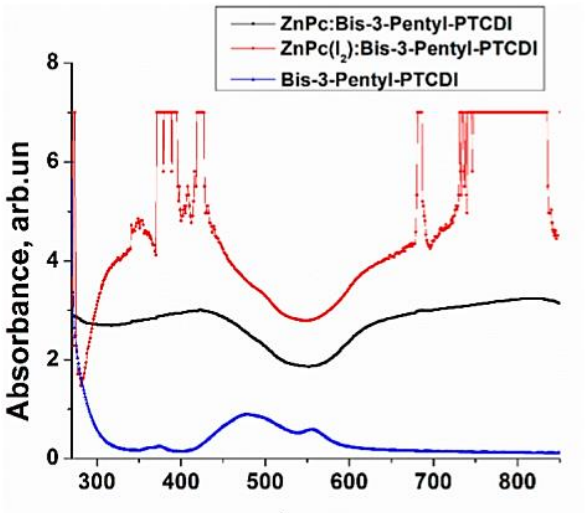



Figure 7. UV-VIS absorption spectra for bis-3-pentyl-PTCDI and mixtures of ZnPc:bis-3-pentyl-PTCDI and ZnPc:$I_2$:bis-3-pentyl-PTCDI in formic acid

For the ZnPc:$I_2$:bis-3-pentyl-PTCDI/FA molecular system, in addition to the characteristic bands for ZnPc, another band with three distinct peaks in the 300-500 nm range stands out, confirming the interaction between ZnPc:$I_2$ and PTCDI. The intensities of the peaks in the absorption spectrum of the ZnPc:$I_2$:bis-3-pentyl-PTCDI mixture in formic acid are somewhat lower than those in the ZnPc:$I_2$/FA spectrum (Figure 7), probably because in dilute solutions the $Zn^{2+}$ ion forms weak complexes with the iodine.

The first part of **Chapter 4** describes the technology for obtaining Schottky-type and bulk heterojunction photovoltaic devices based on processed thin films. Then the electrical properties of Schottky diode ITO/PEDOT:PSS/ZnPc/Al and bulk heterojunction ITO/PEDOT:PSS/ZnPc: PTCDI/Al structures with both doped and undoped ZnPc films are presented. For the interpretation of the experimental data of both types of realized devices, the space charge limited current model was used. To determine the mechanism of current flow through the investigated structures, the direct branches of the J-U characteristic in logarithmic scale were studied. When applying voltage above 0,6 and 1,0 V the Schottky barrier effect disappears (Figure 8). Two linear slopes are observed, confirming different transport mechanisms of the electric charge carriers when applying different values of the direct voltage. At direct bias, the slopes of the characteristics in the low-voltage range up to about 1 V indicate the value of *m* of the order of unity and, therefore, the transport mechanism is Ohmic conduction. When applying voltages higher than 1 V the voltage

current density dependence is quadratic and the conduction mechanism of space charge limited currents with exponential distribution of capture states predominates.

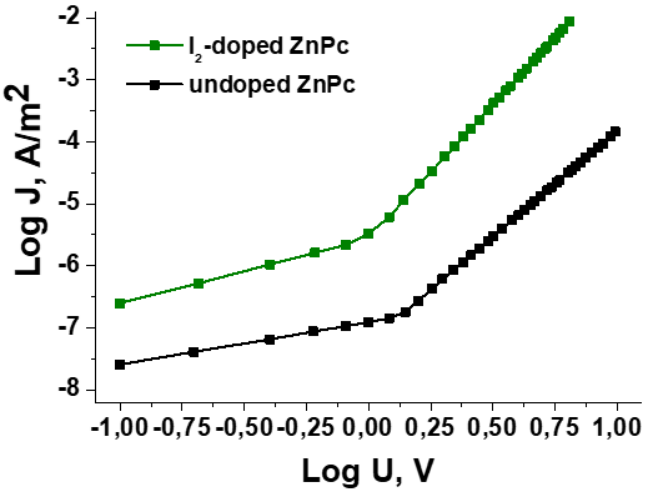



Figure 8. *J-U* characteristic of the direct logarithmic-scale branch of the ITO/PEDOT:PSS/ZnPc/Al structure with iodine-doped and undoped ZnPc film.

Investigation of the logarithmic scale voltage current dependence of ITO/PEDOT:PSS/ ZnPc:PTCDI/Al structures in the measurement temperature range (90...295) K indicates, that at high temperatures the conduction mechanism can be described by the space charge limited current model on traps with carriers moving through the extended states. At low temperatures, transport is governed by the mobility model with charge carriers moving through localized states.

**Chapter 5** covers the study of the photoelectric properties of ITO/PEDOT:PSS/ZnPc Schottky diode structures and ITO/PEDOT:PSS/ZnPc:PTCDI/Al bulk heterojunctions. Initially the formation mechanism and the role of the interfacial aluminium oxide film is described. Figure 9 shows the SEM image of the cross-section (a) and energy diagram schematic (b) of the Schottky diode photovoltaic device.

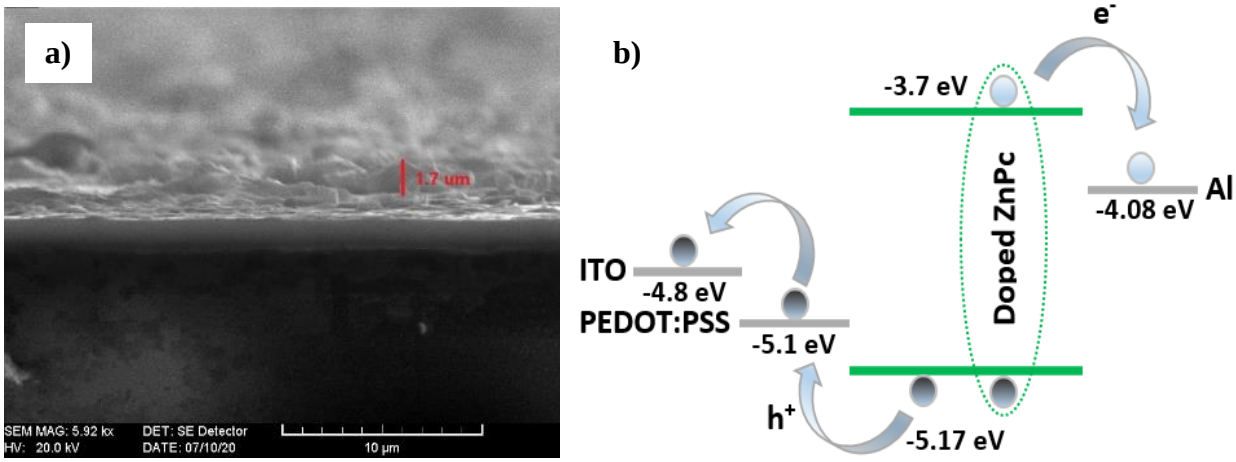



Figure 9. SEM cross-section image (a) and energy diagram schematic (b) for the solution processed glass/ITO/PEDOT:PSS/ZnPc/Al photovoltaic device. [18]

The J-U characteristics of the devices under illumination were measured by applying a voltage to the device, with positive polarity to ITO and negative polarity to aluminium (Al). Figure 10 shows the J-U characteristics of the device measured under AM1.5 (100 mW / $cm^2$), 300K conditions. The $U_{OC}$ values of the ZnPc-based devices with thicknesses of 8,0 µm and 6,2 µm according to the experimental data shown in the figure are 1,03 V and 0,97 V, respectively.

We attribute this high open circuit voltage to: (1) the reduction of surface state formation, (2) the reduction of electrode diffusion, (3) the reduction of electrical charge carrier tunneling mechanism losses across the interface, and (4) the appearance and subsequent presence of the interfacial aluminum oxide film.

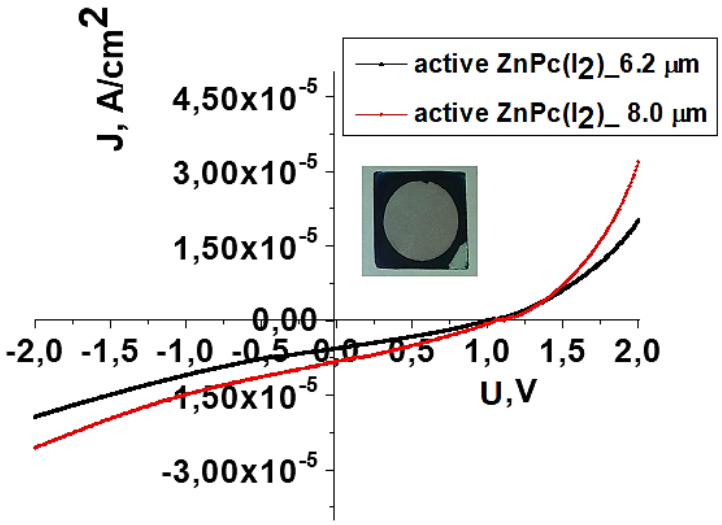



Figure 10, J-U characteristic for glass/ITO/PEDOT:PSS/ZnPc:$I_2$/Al solution processed photovoltaic device.

The PV parameter values for the best devices are shown in Table 3.

Table 3. $U_{OC}$, $J_{SC}$, *FF* and $\eta$ photovoltaic parameters for ZnPc:$I_2$/FA based Schottky type devices of thicknesses 8 µm and 6.2 µm.

| **Photovoltaic parameters** | **Thermal evaporation method** [9] | **Drop method (8.0 µm and 6.2 µm thick devices, respectively)** | |
|---|---|---|---|
| ***UOC* (V)** | 0,89 | 1.03 | 0.97 |
| ***JSC* (µA•cm$^{-2}$)** | 2,8 | 8.2 | 5.6 |
| ***FF*** | | 0.35 | 0.23 |
| ***η, %*** | | 0.3 | 0.125 |

The schematic of the bulk heterojunction-based photovoltaic device and its energy diagram are shown in Figure 11.

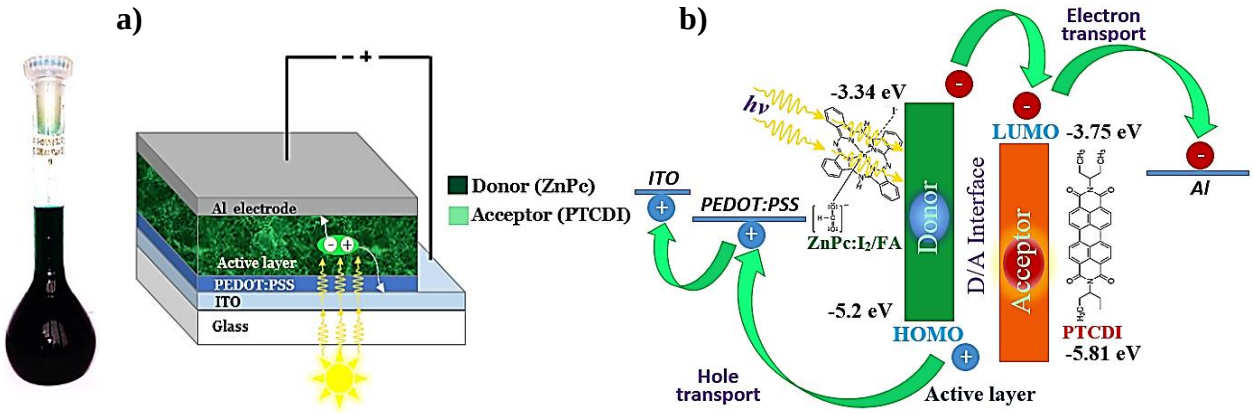



Figure 11. Schematic (a) and energy diagram (b) of the glass/ITO/PEDOT:PSS/ZnPc:PTCDI/Al solution processed photovoltaic device.

Figure 12 shows the current-voltage characteristics of the ITO/PEDOT:PSS/ZnPc:$I_2$:PTCDI/Al devices depending on the volume of $I_2$-doped ZnPc:PTCDI solution used for thin film deposition (film thickness). By studying the current-voltage characteristics at illumination, the short-circuit current $I_{sc}$, open-circuit voltage, $U_{OC}$, series resistance $R_s$, shunt resistance $R_{sh}$, diode factor $n$ were determined. Knowledge of these parameters makes it possible to elucidate physical processes and direct them. The photovoltaic parameters are presented in Table 4.

We see that as the thickness of the film increases, the voltage of the open circuit initially decreases and then starts to increase. The short circuit current density increases with increasing thickness (amount of solution) and at the highest thickness it drops sharply to 4.6 mA/cm$^2$. This current corresponds to the highest open circuit voltage of 0.62 V.

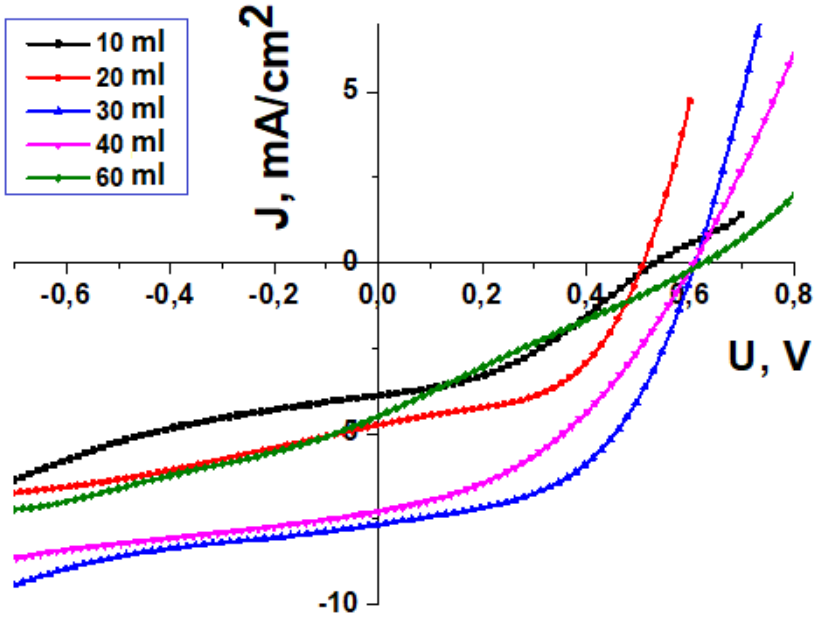



Figure 12. Current-voltage characteristics of ITO/PEDOT:PSS/ZnPc:$I_2$:PTCDI /Al structures of different thicknesses.

Table 4 Photovoltaic parameters $J_{SC}$, $U_{OC}$, FF and η of ITO/PEDOT:PSS/ ZnPc:$I_2$:PTCDI/Al structures as a function of film thickness (solution volume) ZnPc:$I_2$:PTCDI

| **Volume of the solution, ml** | **$J_{SC}$, mA/cm$^2$** | **$U_{OC}$, V** | **FF, %** | **η, %** | **$R_S$, Ohm· cm$^2$** | **$R_{SH}$, Ohm· cm$^2$** |
|---|---|---|---|---|---|---|
| 1 | 3.9 | 0.53 | 37,2 | 0,8 | 113,2 | 529,0 |
| 2 | 4.7 | 0.51 | 50,9 | 1,2 | 21,0 | 307,9 |
| 3 | 7.6 | 0.61 | 51,3 | 2,4 | 19,8 | 458,8 |
| 4 | 7.3 | 0.60 | 40,9 | 1,8 | 35,1 | 405,7 |
| 6 | 4.6 | 0.62 | 24,8 | 0,7 | 109,3 | 161,1 |

In order to improve the photovoltaic parameters, future research intends to deposit, by thermal evaporation, a thin film (1-5 nm) of Ag between ZnPc (doped, undoped and / or combined with PTCDI)/FA and the aluminium electrode. Such a film, analogous to lithium fluoride, on the one hand blocks the migration of oxygenated anionic species from the semiconductor film to the aluminium cathode and thus prevents its oxidation, and on the other hand acts as a more efficient collector and electron transport film. At the same time, according to theoretical estimates, such a film should also contribute to increasing the open circuit voltage. According to initial estimates, the introduction of Ag between the ZnPc:$I_2$:PTCDI film and Al would increase the open circuit voltage from 0.62V to 0.73V. The short-circuit current density would decrease from 7.6 mA/cm$^2$ to 6.82 mA/cm$^2$. The solar-to-electricity conversion efficiency, improving by only 0.1%, would reach 2.5%.

The process of converting solar energy into electrical energy using bulk heterojunction structures can be described as follows: 1) absorption of a photon leads to the formation of an excited state, the creation of the „electron-hole" pair (exciton); 2) diffusion of the exciton to a region where dissociation / separation occurs, and 3) transport of electric charge carriers through semiconductors to the corresponding electrodes. The open circuit voltage that occurs is the direct result of the deviation from the thermodynamic equilibrium state due to the displacement of charge carriers, generated by solar radiation, under the action of local fields, which in the case of organic semiconductors is due to the change in chemical composition [19]. Research [20] has shown that the transfer of photo-induced charge into such a compound takes place in a femtosecond time, much shorter than in other similar processes. In addition, separated charges in such compounds are metastable at low temperatures. The loads arising must be transported to the appropriate electrodes during the lifetime. Charge transport is affected by recombination on the way to the electrodes, especially if electrons and holes (vacancies) are transported through the same material [19]. The charge carriers are extracted from the device through two electrical contacts. An oxide contact, ITO, with work output of about 4,8 eV matches the HOMO level of ZnPc (gap contact), and an

aluminum contact with 4,3 eV work output matches the LUMO of the PTCDI acceptor (electron contact).

Another important parameter of photovoltaic devices is the external quantum efficiency (EQE). The quantum efficiency Q(λ) is defined as the number of generated and separated electron-hole pairs n(λ) per total number of incident photons N(λ) absorbed on the sample surface under short-circuit conditions. The external quantum efficiency (EQE) of the ITO/PEDOT:PSS/ ZnPc:$I_2$:PTCDI/Al structure with different thicknesses of the mixed film is illustrated in Figure 13. The range of photosensitivity is between 300 nm and 800 nm wavelengths. The photosensitivity of the ITO/PEDOT:PSS/ZnPc:$I_2$:PTCDI/Al structure is highest in the range from 450 nm to 800 nm, and with increasing thickness of the absorber film the external quantum efficiency decreases.

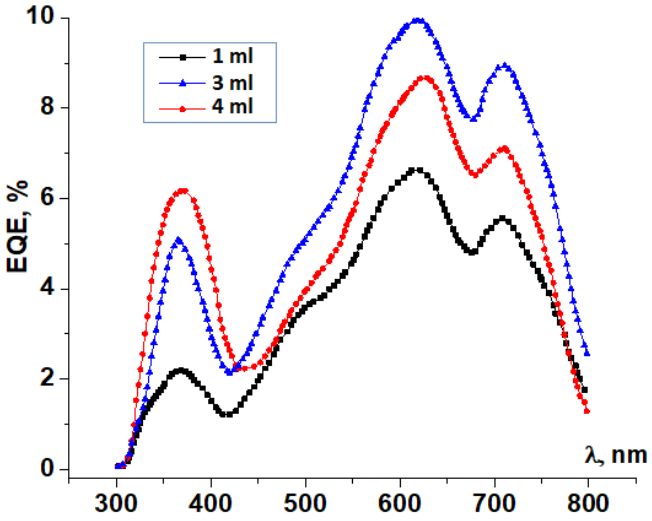



Figure 13. External quantum efficiency (EQE) of the ITO/PEDOT:PSS/ZnPc:$I_2$:PTCDI/Al structure

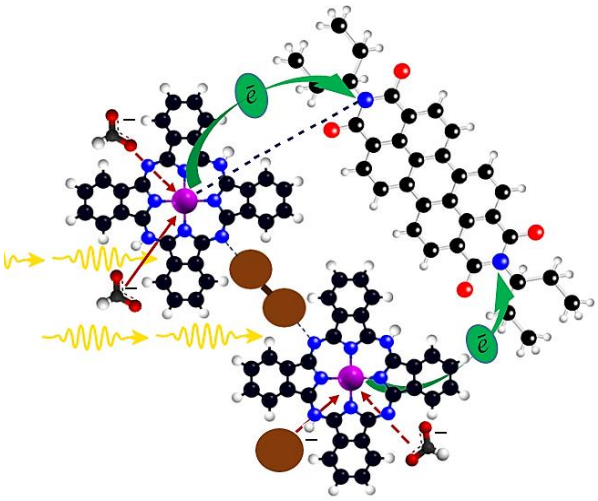


Figure 14. Schematic of the electronic transfer from the ZnPc$(HCOOH)_xI_y$ supramolecular complex (donor) to the active Bis 3-Pentyl PTCDI component (acceptor) during device illumination. [21]

We assume that the higher $J_{SC}$ values for the given devices are due to electron transfer from the supermolecular ZnPc$(HCOOH)_x$ or ZnPc$(HCOOH)_xI_y$ complexes, acting as electron donors (Figure 14), to the active Bis 3-Pentyl PTCDI component (acceptor) during light penetration and absorption in the semiconductor film of the photovoltaic device [21].

## GENERAL CONCLUSIONS

1. ZnPc was synthesized from the solution of phthalonitrile and nitrobenzene, $ZnCl_2$, molybdenum oxide and DBU. The cure was carried out by sublimation of zinc phthalocyanine at a residual pressure of $10^{-3}$ mm Hg and temperature of 500°C. The structure was demonstrated using FTIR spectroscopy by the presence of the most intensive vibration located at 715.14 $cm^{-1}$ and others by comparison with those present in the procured ZnPc powder.
2. As a result of analysis and research, formic acid (FA) was selected as the solvent for the synthesis of zinc phthalocyanine (ZnPc) thin films processed from solutions. The solubility measurement protocol was developed using the absorption spectrum of the synthesized solution. The solubility of ZnPc in FA (98%), the concentration of the saturated solution and the molar extinction coefficient were determined. The molar concentration value for the saturated ZnPc/FA solution is 4,32 $mol \cdot m^{-3}$ and the $\varepsilon_\lambda$ is $1.85 \cdot 10^5 L \cdot mol^{-1} \cdot cm^{-1}$.
3. Different ZnPc/FA solutions of concentrations 0,0432 – 4,32 mol $\cdot m^{-3}$ were prepared for further clarification of nucleation and growth processes. Saturated solutions of ZnPc/FA, (ZnPc +$I_2$)/FA, (ZnPc + PTCDI)/FA and (ZnPc + $I_2$ + PTCDI)/FA were prepared for the synthesis of semiconducting thin films by the centrifugation method and the drop method.
4. The estimated value of the diffusion coefficient *D,* for ZnPc/FA reaches $2.42 \times 10^{-10}$, and the value of the Sherwood number is $6.9 \times 10^{-3}$. According to the data obtained, the particle diffusion rate dominates the solvent evaporation rate in the deposited films.
5. Thin semiconductor films with thicknesses of 2.1 - 8 μm were synthesized for subsequent AFM, XRD, FTIR, RAMAN, XPS, UV-VIS measurements. The analysis of nucleation and growth mechanisms in thin films obtained by spinning and drop method from TCN, DNT, EMLD and DFT perspectives indicates that the nucleation process is heterogeneous and takes place at the substrate surface or on impurities present in the liquid system.
6. The morphology of the synthesized thin films was studied based on AFM and SEM images. Based on the solute-solute and solute-substrate interaction model, the intermolecular and substrate interaction mechanisms of ZnPc and PTCDI molecules, their intensity and privileged directions in nucleation and growth processes were analyzed and discussed. Van der Waals – type interactions between ZnPc molecules ($k_{mm}$) are of the same order of magnitude as the interactions between ZnPc molecules and substrate ($k_{ms}$), but the interactions of the ZnPc molecules, perpendicular to the molecular planes, are more pronounced.

7. XRD structural analysis revealed the impact of FA solvent on the resulting ZnPc molecules with the formation of ZnPc-formate complexes. Increasing the thickness of the thin films from 2.1 μm to 8 μm contributes to a slight increase in crystallite size from ~50 Å to ~256 Å due to the association of a higher number of particles at supersaturation and additional adsorption of growth units to nanogranules in the deposited preliminary film.
8. Iodine doping contributes to structural rearrangement and formation of $ZnPcI_x$, $ZnPc(HCOO^-)_xI_y$ complexes. In the temperature range 200 - 300 $^oC$ the transition of ZnPc into the stable β phase and the removal of PTCDI from the iodine undoped thin films occurs.
9. FTIR analysis confirmed the binding of hydrogen cations, formed upon FA dissociation, to the nonpyrrolic nitrogen atoms in the ZnPC molecule and desorption of formate ions from the central zinc ion at temperatures above 300 $^oC$. Raman analysis confirmed the removal of molecular iodine from doped thin films at temperatures above 100 $^oC$.
10. XPS analysis confirmed the presence of the triiodide ion $I_3^-$ in the synthesized thin films and the connection of iodine with zinc in the ZnPc molecule (signal at 619, 8 eV), thus authenticating the proposed particle interaction mechanisms.
11. Both undoped and iodine-doped ZnPc films form Schottky barriers with Al and ITO contacts. The rectification coefficient increases with iodine doping of ZnPc. For the ITO/PEDOT:PSS/ZnPc/Al structure with the $I_2$-doped ZnPc film, the resistance $r_d = 9 \cdot 10^3$ $\Omega \cdot m^2$, and for the undoped film it reaches $3.8 \cdot 10^4$ $\Omega \cdot m^2$.
12. When directly biasing ITO/PEDOT:PSS/ZnPc/Al structures with both $I_2$-doped and undoped ZnPc film, in the voltage range up to nearly 1 V the value of *m is* of the order of unity, indicating an Ohmic conduction mechanism, and when applying voltages higher than 1 V the voltage current density dependence is quadratic $J \sim U^n$ and the conduction mechanism is space charge limited current.
13. From the temperature dependence of the conduction current at voltages lower than the transition voltage value, a region with activation energy $E_a$=0.03 eV corresponding to the band conduction mechanism is distinguished.
14. In the temperature range 160K - 295 K, the experimental data set is better described with the space charge limited current model on traps. The parameter values in this case are $\mu = 6.2 \times 10^{-6}$ $cm^2$ $V^{-1}$ $s^{-1}$, $N\nu = 1.0 \times 10^{19}$ $cm^{-3}$, and the total density of capture states $N_t = 5.0 \times 10^{17}$ $cm^{-3}$.
15. For the temperature range 90 K to 160 K the mobility model is used which is in full agreement with the experimental data, with the parameters: $\mu_0 = 8.23 \times 10^{-13}$ $cm^2$ $V^{-1}$ s, $\gamma = 5.4 \cdot 10^{-5}$ eV $cm^{-1/2}V^{-1/2}$ and $\Delta_0$=0.040 eV.

16. At high temperatures the conduction mechanism for ITO/PEDOT:PSS/ZnPc:PTCDI/Al devices can be illustrated by the space charge limited current model on traps with carriers moving through extended states. At low temperatures, transport is governed by the mobility model with charge carriers passing through localized states.
17. Glass/ITO/PEDOT:PSS/ZnPc/Al Schottky diode and glass/ITO/PEDOT:PSS/ZnPc: PTCDI/ Al volume heterojunction photovoltaic devices with both undoped and $I_2$-doped ZnPc film were obtained and the photovoltaic parameters were estimated. The FF values are significantly affected by the high values of the series resistances in the semiconductor films processed from chemical solutions.
18. The realization of Schottky glass/ITO/PEDOT:PSS/ZnPc/Al diode photovoltaic devices from chemical solutions indicates open circuit voltage about 1.03 V, almost equal to the theoretical value. ITO/PEDOT:PSS/ZnPc ($I_2$)/Al photovoltaic devices have a higher efficiency than those obtained by the vacuum evaporation method, equal to 0.3 %.
19. The higher values (on the order of milliamperes/cm$^2$) of $J_{SC}$ for bulk heterojunction devices are due to electron transfer from the supramolecular complexes ZnPc$(HCOOH)_x$ or ZnPc$(HCOOH)_xI_y$, acting as electron donors, to the active component Bis 3-Pentyl PTCDI (acceptor) during device illumination.
20. Glass/ITO/PEDOT:PSS/ZnPc:PTCDI/Al volume heterojunction photovoltaic devices achieved a solar-to-electricity conversion efficiency of 2.4 %.

**RECOMMENDATIONS:**

- Introduction of transparent, conductive electrodes on both sides to use not only sunlight but also indoor light, which will make these cells very attractive for powering low-power devices;
- Deposition, by thermal evaporation, of a thin (1-5 nm) film of LiF between ZnPc (doped, undoped and / or combined with PTCDI/FA and the aluminium electrode. Such a film, on the one hand blocks the migration of oxygenated anionic species from the semiconductor film to the aluminium cathode and thus prevents its oxidation, and on the other hand acts as a more efficient collector and electron transport film. At the same time, this would significantly improve the quality of the contact between the Al electrode and the active film of the devices;
- Use of organic and inorganic semiconductor tandem in the production of photovoltaic devices;
- Functionalisation of the PTCDI material to lower its LUMO level, preserving its electron accepting properties. This would help increase the energy gradient in the interface region, amplifying the driving force of exciton dissociation.

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21. T. Potlog, V. Furtuna, I. Lungu, T. Masuzawa, H. Mimura, Physical-Chemical Properties Of Self-Assembled Structures In Solution Of Zinc Phthalocyanine And Bis-3-Pentyl-PTCDI Derivative, The Journal Of Physical Chemistry C. 17 (2020) 9470-9483.

## LIST OF SCIENTIFIC PUBLICATIONS ON THE THESIS TOPIC

**Articles in international journals with impact factor**

1. POTLOG, T., **FURTUNA, V.**, LUNGU, I., MASUZAWA, T., MIMURA, H. Physical-Chemical Properties of Self-Assembled Structures in Solution of Zinc Phthalocyanine and Bis-3-pentyl-PTCDI Derivative. In: *The Journal of Physical Chemistry C*. 2020, 124(17) pp. 9470-9483, DOI: 10.1021/acs.jpcc.9b11605.
2. POTLOG, T., **FURTUNA, V.**, LUNGU, I., ROBU, S., DRAGALINA, G., POPUSOI, A., BULMAGA, P. Synthesis and Characterization of CuPc-PEPC Composite Thin Films and Photovoltaic Devices by Drop Casting Method. In: *Materiale Plastice.* 2020, nr. 57(4), pp. 134-144. ISSN Print 0025-5289, ISSN Online 2668-8220

**Articles in national journals of category B**

3. **FURTUNĂ, V.**, DUCA, D., POTLOG, T. Straturi Nanostructurate de ZnO Dopate cu Al Pentru Fotoelectrozi în Structurile Hibride pe Baz Ftalocianinei de Cupru. In: *Studia Universitatis Moldaviae*. 2016, nr. 2(92), pp. 30-39. ISSN 1857-2073, ISSN Online 2345-1033.
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**Contributions (articles, abstracts, theses) to conference materials and other scientific papers.**

6. POTLOG, T., **FURTUNA, V.**, ROTARU, C., RUSNAC, R., ROBU, S., MIMURAM H. Material Properties of Zinc Phthalocyanine from FA Solution and Application in Organic Solar Cells. In: *The International Journal of Industrial Electronics and Electrical Engineering*. 2018, Volume-6, Issue-1, pp. 40 – 46. ISSN(p): 2347-6982, ISSN(e): 2349-204X.
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13. LUNGU, Ion, **FURTUNĂ, Vadim**, POPUȘOI, Ana, POTLOG, Tamara, DRAGALINA, Galina, ROBU, Ștefan. Photosensitive Thin Films Based on Carbasole Polymers and Meta-lophtalocyanines. In: *The Scientific Bulletin Addendum №3/2018 of The International Student Innovation and Scientific Research Exhibition „CADET INOVA'18",* April 19-21, 2018, Sibiu, Romania, pp. 251-252. ISSN 2501-3157.
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30. I. Gadiac, **V. Furtună** and T. Potlog, "Fabrication of a ITO/PEDOT:PSS/ZnPc:I2/Al Schottky diode solar cells using Solution Technique," *2021 International Semiconductor Conference (CAS)*, 2021, pp. 195-198, doi: 10.1109/CAS52836.2021.9604121.

## ADNOTARE

la teza de doctorat **„Elaborarea dispozitivelor fotovoltaice pe baza semiconductorilor organici/ anorganici”** prezentată de către **Furtună Vadim,** pentru conferirea titlului ştiinţific de doctor în ştiinţe fizice, specialitatea **134.01 „Fizica şi Tehnologia Materialelor”**, Chişinău, 2021.

**Structura tezei:** Teza constă din introducere, 5 capitole, concluzii generale și recomandări, 243 surse bibliografice, 146 pagini de text de bază, 93 figuri, 16 tabele și 4 anexe (cu 6 figuri, 2 formule). Rezultatele prezentate în teză au fost publicate în 30 lucrări ştiinţifice: 7 articole (dintre care 2 în reviste internaționale cu factor de impact) și 23 rezumate la conferințe științifice internaționale.

**Cuvinte cheie:** ZnPc, acid formic, PTCDI, iod, heterojoncţiune în volum, structură de tip Schottky, celulă solară, interfaţă, conversia energiei solare, parametri fotovoltaici.

**Domeniul de cercetare:** Materiale organice şi structuri pentru fotovoltaică, Fizica şi Tehnologia Materialelor.

**Scopul lucrării:** Elaborarea şi optimizarea tehnologiei de sinteză din soluții chimice, prin metoda centrifugării și metoda picăturii, a straturilor subțiri pe baza ftalocianinei de zinc, precum și studierea proprietăților structurale și optice ale straturilor obținute, pentru implementarea lor în producerea dispozitivelor fotovoltaice.

**Obiectivele cercetării:** Elaborarea protocolului de solubilizare a ZnPc și PTCDI; optimizarea regimurilor de sinteză și dopare a straturilor subțiri din soluții chimice, în vederea controlului proprietăţilor acestora pentru aplicaţii în fotovoltaică; investigarea corelaţiilor existente între microstructură şi proprietăţile optice; optimizarea tehnologiei de obținere a dispozitivelor fotovoltaice.

**Noutatea şi originalitatea ştiinţifică a lucrării**: Elaborarea și optimizarea regimurilor de sinteză a straturilor subțiri din soluții pe bază de ZnPc şi PTCDI în FA, precum și a celor de dopare *in situ* a acestor straturi cu $I_2$; obținerea în premieră, din soluții, a dispozitivelor fotovoltaice de tipul diodei Schottky ITO/PEDOT:PSS/ZnPc:$I_2$/Al cu valoarea tensiunii de circuit deschis 1.03 V, care e mai înaltă decât în cazul dispozitivelor obținute prin evaporare termică în vid; obținerea în premieră a dispozitivelor fotovoltaice, din soluții, de tipul heterojoncțiune în volum ITO/PEDOT:PSS/ZnPc:$I_2$: PTCDI/Al cu randament de conversie 2.4 %; elucidarea mecanismelor de interacțiune dintre solvent (FA), substanțele active(ZnPc, PTCDI) și dopant ($I_2$) în baza studiului complex al proprietăților morfologice, structurale, vibraționale și optice; stabilirea mecanismelor de transport al purtătorilor de sarcină prin dispozitivele realizate, cercetate la aplicarea câmpului electric și iluminare.

**Problema ştiinţifică soluţionată** în această teză de doctorat este elaborarea tehnologiei de fabricare cu costuri de producție reduse a celulelor solare organice pe bază de ZnPc și ZnPc:PTCDI, elucidarea principiilor fizice de funcționare și găsirea de soluții pentru creșterea eficienței de conversie a energiei solare în energie electrică.

**Semnificaţia teoretică a lucrării** constă în elucidarea proceselor fizice, care permit controlul efectiv asupra nucleației şi creşterii straturilor subțiri din soluții chimice, formarea interfeţei structurilor pe baza de ZnPc, de tip dioda Schottky și de tip heterojoncțiune ZnPc:PTCDI și clarificarea nuanţelor procesului de transfer de sarcină electrică de la interfaţa structurilor.

**Valoarea aplicativă** constă în elaborarea și optimizarea tehnologiei de preparare a structurilor pe baza de ZnPc de tip diodă Schottky și de tip heterojoncțiune în volum ZnPc:PTCDI (atât nedopate cât și dopate cu iod) cu o eficienţă de conversie mai mare decât cea a dispozitivelor obținute prin evaporare termică în vid înalt.

**Implementarea rezultatelor:** Rezultatele ştiinţifice obţinute pot fi implementate în procesul instructiv-educativ la Institutul de Cercetare şi Inovare al Universității de Stat din Moldova.

## ANNOTATION

of the doctoral thesis **"Development of photovoltaic devices based on organic/inorganic semiconductors"**, presented by **Furtuna Vadim** for conferring the scientific title of Doctor in Physics, specialty **134.01- "Physics and Material's Technology"**, Chisinau, 2021.

**The structure of the thesis:** The thesis consists of introduction, 5 chapters, general conclusions and recommendations, 146 basic text pages, 243 bibliographic sources, 16 tables, 93 figures and 4 annexes. The obtained results are published in 30 scientific papers: 7 articles (2 of wich are published in international journals with IF) and 23 abstracts at international scientific conferences.

**Keywords:** ZnPc, formic acid, PTCDI, iodine, bulk heterojunction, Schottky diode, solar cell, interface, solar energy conversion, photovoltaic parameters.

**Field of research:** organic materials and structures for photovoltaics, Physics and Technology of Materials.

**The goal of the thesis:** The development and the optimization of the technology of ZnPc based thin films synthesis from chemical solutions, by spin coating and drop casting methods, as well as the study of structural and optical properties of the obtained layers for its implementation in the production of photovoltaic devices.

**The objectives of the thesis**: The development of the protocol of solubilization for ZnPc and PTDCI; optimization of the synthesis and doping regimes of the thin films in order to control their physical properties for photovoltaic applications; the investigation of the correlations between microstructure and optical properties; the optimization of the technological regime for fabrication of the photovoltaic devices.

**Novelty and scientific originality**: The development and the optimization of ZnPc and PTCDI thin films synthesis regimes from chemical solution, as well as *in situ* iodine doping regimes of these layers; synthesis for the first time, from solutions, of photovoltaic devices based on ITO/PEDOT:PSS/ ZnPc:$I_2$/Al Schottky diode with the value of open circuit voltage 1.03 V, higher than in the case of devices obtained by thermal evaporation in vacuum; The obtaining for the first time of the photovoltaic devices based on ITO/PEDOT:PSS/ZnPc:$I_2$:PTCDI/Al bulk heterojunction with conversion efficiency 2.4%; elucidation of the interaction mechanisms between the solvent (FA), the active substances (ZnPc and PTCDI) and the dopant ($I_2$) based on the complex study of morphological, structural, vibrational and optical properties; establishing of the transport mechanisms of the electrical carriers through the developed devices at the application of the electric field and light.

**Scientific problem solved** in this doctoral thesis is the development of manufacturing technology with low production costs of organic solar cells based on ZnPc and ZnPc: PTCDI, the understanding of the physical principles of operation and the finding of solutions to increase the efficiency of solar energy conversion of the devices.

**The theoretical significance of the thesis** consists in elucidating the physical processes which allow effective control over nucleation and growth of thin layers from chemical solutions, the controlled formation of the interface of structures based on ZnPc Schottky diode and ZnPc:PTCDI bulk heterojunction, and clarifying the nuances of electric charge transfer process from the interface**.**

**The applicative value of the thesis** consists in the elaboration and optimization of the technology of the preparation of ZnPc Schottky diode and ZnPc: PTCDI bulk heterojunction devices with a higher conversion efficiency compared to the efficiency of the devices obtained by thermal evaporation in high vacuum.

**Implementation of the results:** The obtained scientific results can be implemented in the educational process at the Research and Innovation Institute of the State University of Moldova.

## АННОТАЦИЯ

диссертации **«Разработка фотовольтаических приборов на основе органических/ неорганических полупроводников»**, представленной **Вадимом Фуртунэ** для присвоения ученой степени доктора физических наук по **специальности 134.01 «Физика и технология материалов»**, Кишинёв, 2021 год.

**Структура диссертации:** Диссертация состоит из введения, 5 глав, общих выводов и рекомендаций, списка литературы из 243 публикаций, 146 страниц основного текста, 93 рисунков, 16 таблиц и 4 приложения. Полученные результаты опубликованы в 30 научных работах: 7 научных статей (2 из которых опубликованы в международных журналах с импакт-фактором) и 23 тезисов на международных научных конференциях.

**Ключевые слова:** ZnPc, муравьиная кислота, PTCDI, иод, объемный гетеропереход, диод Шоттки, граница раздела, преобразование солнечной энергии, фотовольтаические параметры.

**Область исследования:** органические материалы и структуры для фотоэлектрической энергетики, физика и технология материалов.

**Цель работы:** разработка и оптимизация технологии синтеза тонких слоев на основе ZnPc из химических растворов, а также исследование структурных и фотоэлектрических свойств полученных слоев для их внедрения в производство фотовольтаических приборов.

**Задачи исследования:** разработка протокола растворимости ZnPc и PTCDI; оптимизация режима синтеза и легирования тонких слоев с целью управления их свойствами для фотоэлектрических применений; исследование корреляции между микроструктурой и оптическими свойствами; оптимизация технологии получения фотовольтаических приборов.

**Новизна и научная оригинальность работы:** разработка и оптимизация режимов синтеза тонких слоев из растворов на основе ZnPc и PTCDI в FA, а также легирования *in situ* данных слоев йодом; впервые получены, из раствора, фотовольтаические устройства на основе диода Шоттки ITO/PEDOT:PSS/ZnPc:$I_2$/Al с величиной напряжения холостого хода 1,03 В, что выше чем у приборов полученных термическим испарением в вакууме и на основе гетероперехода ITO/PEDOT:PSS/ZnPc:$I_2$:PTCDI/Al с эффективностью преобразования 2,4%; определены механизмы взаимодействия между растворителем (FA), активными веществами (ZnPc, PTCDI) и примесью ($I_2$); установлены механизмы токопрохождения через разработанные приборы, при изменении электрического поля и освещении.

**Решённая научная проблема:** разработана технология производства органических солнечных элементов с низкими затратами на основе тонких слоев ZnPc и ZnPc:PTCDI, установлены физические принципы работы и найдены решения для повышения эффективности преобразования солнечной энергии.

**Теоретическая значимость работы** состоит в выяснении физических процессов, позволяющие контролировать образование зародышей и рост тонких слоев из химических растворов, формировать границ раздела кристаллитов и процесс переноса электрического заряда через границ раздела.

**Прикладное значение** состоит из разработки и оптимизации технологии изготовления фотовольтаических приборов на основе ZnPc, диода Шоттки и объемного гетероперехода ZnPc:PTCDI (легированных и нелегированных йодом), с более высокой эффективностью преобразования по сравнению с эффективностью устройств полученных термическим испарением в высоком вакууме.

**Внедрение научных результатов:** полученные научные результаты могут быть внедрены в учебно-образовательный процесс в Молдавском госуниверситете.

**FURTUNĂ, Vadim**

# DEVELOPMENT OF PHOTOVOLTAIC DEVICES BASED ON ORGANIC/INORGANIC SEMICONDUCTORS

SPECIALITY 134.01 – MATERIALS PHYSICS AND TECHNOLOGY

**PhD in Physical Sciences thesis summary**

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