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Doctoral Program in Environmental Science

PHOTOELECTRICAL PROPERTIES OF INNOVATIVE ORGANIC MATERIALS FOR SOLAR CELLS

Summary of doctoral thesis

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This dissertation is proposed for obtaining the doctoral degree in Environmental Engineering and will be defended on 28th August, 2015 at 14.00 at the Faculty of Power and Electrical Engineering of the Riga Technical University, Riga, 12/1 Azenes Street, room No. 115.

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CONFIRMATION STATEMENT

I, the undersigning, hereby confirm that I have developed this dissertation submitted for consideration at Riga Technical University for obtaining the doctoral degree in Environmental Engineering. This study has not been submitted to any other university or institution for the purpose of obtaining scientific degree.

Jānis Latvels _____

Date: 20.07.2015.

This dissertation is written in Latvian and contains: introduction, 4 chapters, conclusions, bibliography, 57 figures, 8 tables and 104 pages. The bibliography contains 151 references.

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Introduction

Renewable and non-polluting energy is one of the biggest challenges of modern society; hence the new energy sources which would provide simple and cost-effective solutions are necessary.

Solar cells are an important alternative energy source, which takes an increasing role in the current distribution of energy production and is a full-fledged replacement for fossil energy. Unlike other forms of energy, solar energy is completely ecological energy source and it does not cause side effects. Furthermore, solar energy can be differentiated – it can be used both – locally for a small device operation and broadly for residential house electricity and heat supply or significant size industrial solar plants with several megawatts of power.

Organic thin films with semiconductor properties nowadays are widely studied as their use in organic electronics or photonics is very promising, including solar cell development. Organic materials have several significant advantages: dimensions of electronic components can be very small, as one molecule acts as an electronic element; manufacturing process has significantly less impact on the environment because the required temperature to create an organic solar cells can be several times reduced compared to silicon based solar cells; cheap and easy recycling; possibility to create flexible devices. Thus, organic materials provide opportunities to expand the use of solar energy.

Material selection is one of the prerequisites to develop organic solar cells. The knowledge of material properties and energy structure can play a crucial role in development of organic solar cells.

In this work indandione containing compounds with different functional groups attached have been investigated. Added groups allowed improving the energy parameters and photovoltaic properties compared with other previously known indandione compounds. Attached tri-phenyl group gives the possibility to make organic solar cells from the solution. The traditional method for making thin films - thermal deposition in vacuum is costly and requires large amounts of energy. Thin films fabrication from solution saves energy and raw materials, particularly when printing or "roll-to-roll" method is applied. Solar cell fabrication from solution is becoming more and more popular, but now it's possible mostly using polymers. Fabrication from solution using low molecular weight compounds instead of polymers is more cost-effective because repeatability of the synthesis of low molecular weight compounds is significantly higher and at the same time recycling process is much easier than of polymers.

The aim and objectives

The aim of the work is to find and investigate innovative materials for organic solar cells possible to use for electricity production.

The following objectives were set in order to achieve the aim of the research:

- Find suitable materials for environmentally friendly solar cells.
- Determine influence of different attached functional groups on the selected material properties.
- Plan an experiment; experimentally determine the photovoltaic properties of selected materials.
- Create prototypes for different types of organic solar cells using selected materials.
- Determine the characteristics that influence efficiency of organic solar cell.

Methodology of the research

The methodology includes two interconnected parts.

The first part consists of selection of materials usable for solar cell development. It also includes investigation of photoelectrical properties of selected materials using space charge limited current method (determination of photocurrent and energetic levels of material). The summary of characterizing parameters of investigated materials has been made based on obtained data.

The second part includes the development of solar cell prototypes using a variety of organic solar cell types – bilayer solar cells, dye sensitized solar cells, bulk heterojunction solar cells. Materials to develop solar cell prototypes were chosen based on previously mentioned summary of characterizing parameters of materials.

The parameters characterizing solar cells were determined for prototypes - short-circuit current, open circuit voltage, fill factor and power conversion efficiency. The dependences of characterizing parameters on investigated materials concentration in prototypes were determined for most promising prototypes.

Scientific novelty

Within the work innovative indandione containing organic compounds have been investigated. The photoelectrical properties of studied materials have been determined and their possible application in development of organic solar cells has been proved. Most suitable materials have been found for various types of organic solar cells – bilayer, dye sensitized and bulk heterojunction solar cells made from solution. Different synthesized compounds absorb light at different wavelengths, allowing them to be combined, thus expanding the solar cell absorption spectrum.

There have been determined energetic values of investigated compounds and correlation between them. It gives new information about this type of materials.

For the first time indandione containing glass structure forming materials with added tri-phenyl groups have been obtained making possible to produce organic solar cells from the solution and build them from the low molecular weight compounds, as well as to avoid the use of polymers in solar cells, thus allowing the use of resources-saving production method from solution. The energetic values and photoelectrical properties were obtained as well as prototypes of organic solar cells were made.

There has been discovered indandione containing material which allows increasing solar cell efficiency in a widely used organic solar cell system P3HT:PCBM by adding it in the system.

Practical significance of the work

This work has a great practical significance. A patent application has been developed and submitted for one of investigated materials which allow improving power conversion efficiency of widely used organic solar cell system. The application of newly synthesized materials which form a glass structure thus significantly reducing energy and costs for solar cell production has been investigated.

The results of work are significant and usable for organic solar cells manufacturing companies to increase the efficiency and reduce the costs and used energy of solar cells being in production. The results are usable also for companies producing raw materials for organic cells to widen the choice of materials usable in energy saving production processes, as well as for broadening organic solar cell industry, increasing choice of usable materials thus promoting industry transition to energy and raw materials saving solar cell production method – soluble materials offered printing technology. The results of work give contribution in research, synthesizing new materials with improved properties on the basis of the studied compounds.

Approbation

The obtained results of the work are reflected in 9 scientific publications. Results of the study have been reported in 21 international conferences and 2 local conferences, the patent application is submitted (P-14-24).

Scientific publications

1. J.Latvels, R. Grzibovskis, K. Pudzs, A. Vembris, "PHOTOVOLTAIC EFFECT IN BULK HETEROJUNCTION SYSTEM WITH GLASS FORMING INDANDIONE DERIVATIVE DMABI-6PH", submitted in Synthetic metals

2. J. Latvels, R. Grzibovskis, K. Pudzs, A. Vembris, D. Blumberga "PHOTOELECTRICAL PROPERTIES OF INDANDIONE FRAGMENT CONTAINING AZOBENZENE COMPOUNDS", SPIE Proceedings, 9137, 91371G, (2014), DOI: 10.1117/12.2052604

3. J. Latvels, R. Grzibovskis, A. Vembris, D. Blumberga "IMPROVEMENT OF EFFICIENCY OF SOLAR PV. POTENTIAL MATERIALS FOR ORGANIC SOLAR CELLS", Environmental and Climate Technologies, 2013, Vol. 12, pp. 28-33

4. S. Popova, K. Pudzs, J. Latvels, A. Vembris "LIGHT EMITTING AND ELECTRICAL PROPERTIES OF PURE AMORPHOUS THIN FILMS OF ORGANIC COMPOUNDS", Optical Materials, 2013, Vol. 36, No 2, pp. 529-534

5. R.Grzibovskis, A.Vembris, J.Latvels "PHOTOVOLTAIC PROPERTIES OF GLASS FORMING PYRANYLIDEN DERIVATIVES IN THIN FILMS", IOP Conference Series: Materials Science and Engineering, 2013, Vol. 49, doi:10.1088/1757-899X/49/1/012055

6. I.Kaulachs, I.Muzikante, L.Gerca, G.Shlihta, P.Shipkovs, G. Kashkarova, M.Roze, J.Kalnachs, A.Murashov, J.Latvels, G.Rozite, "ELECTRODE INFLUENCE ON BI-LAYER BULK HETEROJUNCTION SOLAR CELL CONTAINIBG P3HT", "26th European Photovoltaic Solar Energy Conference and Exhibition" – Hamburg (Germany) 26th EU PVSEC Proceedings on DVD, (2011) pp 601-604.

7. M. Indrikova, J. Latvels, I. Muzikante, B. Turovska, "PHOTOELECTRICAL PROPERTIES AND ENERGETICAL STRUCTURE OF THIN FILMS OF INDANDIONE DERIVATIVES", "*Material Science (MEDŽIAGOTYRA)*", 2011, Vol. 17, No. 2. 2011, pp. 125-131

8. R.Grzibovskis, J.Latvels, I.Muzikante, „PHOTOELECTRICAL PROPERTIES OF THIN FILMS OF DMABI DERIVATIVES", *IOP Conf. Series: Materials Science and Engineering,* 2011, Vol.23, 012021 doi:10.1088/1757-899X/23/1/012021

9. A.Vembris, M. Porozovs, I.Muzikante, J. Latvels, A. Sarakovskis, V. Kokars, E. Zarins, „NOVEL AMOURPHOUS RED ELECTROLUMINESCENCE MATERIAL BASED ON PYRANYLIDENE INDENE-1,3-DIONE DERIVATIVE" , *„Latvian Journal of Physics and Technical Sciences",* 2010, Vol. 47, No 3, pp.23-30

Reports in international conferences

1. Advanced optical materials and devices AOMD-8, "PHOTOELECTRICAL PROPERTIES OF GLASS FORMING INDANDIONE DERIVATIVE DMABI-6PH FOR ORGANIC SOLAR CELLS", August 25-27, 2014, Riga, Latvia

2. The 10th International Conference on Organic Electronics, "PHOTOVOLTAIC PROPERTIES OF AMORPHOUS STRUCTURE FORMING AZOBENZENE COMPOUNDS CONTAINING INDANDIONE FRAGMENT", June 11-13, 2014, Modena, Italy

3. SPIE Photonics Europe 2014, "PHOTOELECTRICAL PROPERTIES OF INDANDIONE FRAGMENT CONTAINING AZOBENZENE COMPOUNDS", April 14-17, 2014, Brussels, Belgium

4. International Scientific Conference Environmental and Climate Technologies, "IMPROVEMENT OF EFFICIENCY OF SOLAR PV. POTENTIAL MATERIALS FOR ORGANIC PHOTOVOLTAIC CELLS", October 14-16, 2013

5. 9th International Conference on Organic Electronics ICOE 2013, „EVALUATION OF N,N'-DIMETILAMINOBENZILIDEN-1,3-INDANDIONEBASED MATERIALS AS POTENTIAL MATERIALS FOR ORGANIC SOLAR CELLS", June 18-20, 2013, Grenoble, France

6. Conference on functional materials and nanotechnologies 2013 "PHOTOELECTRICAL PROPERTIES OF DMABI DERIAVATIVES AS MATERIALS FOR SOLAR CELLS", April 21-24, 2013, Tartu, Estonia

7. Advanced Materials and Technologies 2012, „CORRELATIONS BETWEEN THRESHOLD VALUE AND OPTICAL ENRGY GAP IN THIN FILMS OF DMABI DERIVATIVES", August 26-31, 2012, Palanga, Lithuania

8. SPIE Photonics Europe 2012, "RELATIONS OF ENERGY LEVELS IN THIN FILMS OF POLAR PHOTOCONDUCTIVE MOLECULES", April 16-19, 2012, Brussels, Belgium

9. Functional materials and nanotechnologies 2012, „ELECTRICAL PROPERTIES AND MORPHOLOGY OF PENTACENE THIN FILMS EVAPORATED ON DIFFERENT TEMPERATURE SUBSTRATE", April 17 – 20, 2012, Riga, Latvia

10. Developments in Optics and Communications 2012, „RELATIONS BETWEEN ENERGY LEVELS AND REDOX POTENTIAL OF DMABI DERIVATIVES", April 12-14, 2012, Riga, Latvia

11. The European Conference on Organized Films 2011, „DETERMINATION OF THE ENERGY STRUCTURE OF INDANDIONE CHROMOPHORES IN THIN FILMS", July 17-20, 2011, Sheffield, UK

12. Electronic, Related Properties of Organic Systems 12th INTERNATIONAL CONFERENCE: „PHOTOELECTRICAL PROPERTIES OF THIN FILMS OF DMABI DERIVATIVES", July 11-13, 2011, Vilnius, Lithuania

13. E-MRS 2011 SPRING MEETING 2011 & E-MRS/MRS BILATERAL CONFERENCE on ENERGY, „DETERMINATION OF THE ENERGY STRUCTURE OF THE SANDWICH-TYPE ORGANIC THIN FILMS", May 9-13, 2011, Nice, France

14. E-MRS 2011 SPRING MEETING 2011 & E-MRS/MRS BILATERAL CONFERENCE on ENERGY, „BI-LAYER GaOHPc:PCBM/P3HT:PCBM SOLAR CELL", May 9-13, 2011, Nice, France

15. 54th Scientific Conference for Young Students of Physics and Natural Sciences Open Readings 2011, „PHOTOELECTRICAL PROPERTIES OF DMABI DERIVATIVES IN THIN FILMS", March 17-19, 2011, Vilnius, Lithuania

16. Functional materials and nanotechnologies, „PHOTOELECTRICAL PROPERTIES OF THIN FILMS OF DMABI DERIVATIVES", April 5 – 8, 2011, Riga, Latvia

17. Baltic Polymer symposium 2010 , „ENERGETIC STRUCTURE INVESTIGATION OF NEW INDANDIONE DERIVATIVES", September 8-11, 2010, Palanga, Lietuva

18. 9th International conference on Global Research and Education Inter-Academia 2010, „INVESTIGATION OF ENERGETIC STRUCTURE OF ORIGINAL INDANDIONE DERIVATIVES", August 9-12, 2010, Riga, Latvia

19. Developments in Optics and Communications 2010, „NEW INDANDIONE TYPE ORGANIC MATERIALS FOR SOLAR CELLS", April 23-25, 2010, Riga, Latvia

20. SPIE Photonics Europe 2010 „NEW INDANDIONE BASED MATERIALS FOR ORGANIC SOLAR CELLS: ELECTRICAL AND PHOTOELECTRICAL PROPERTIES", April 12-16, 2010, Brussels, Belgium

21. Functional materials and nanotechnologies, „PHOTOELECTRICAL PROPERTIES OF INDANDIONE MONO- AND MULTISTRUCTURED THIN FILMS", March 16-19, 2010, Riga, Latvia

Reports in local conferences

1. LU CFI 28. Scientific conference, "PHOTOCONDUCTIVITY PROCESSES IN POLYCRYSTALLINE FILMS OF DMABI DERIVATIVES", February 8-10, 2012, Riga, Latvia

2. LU 68. Conference, session „New scientists in Environmental sciences", „NEW MATERIALS FOR ORGANIC SOLAR CELLS", February 3, 2010, Riga, Latvia

Structure of the thesis

This dissertation is written in Latvian and contains: introduction, 4 chapters, conclusions, bibliography, includes 57 figures, 8 tables. It has 104 pages. The bibliography contains 151 references. In this summary literature review and bibliography are not included.

1. ENVIRONMENTAL IMPACT ASSESSMENT OF ORGANIC SOLAR CELLS

Organic solar cells have reached a level of development to be able to consider as a possible alternative energy resource. There has been progress since low cost solar cell technology with reported efficiency of one percent was first mentioned in the early nineties. In recent years, organic solar cell development has expanded rapidly. Organic solar cells offer several advantages: low manufacturing costs, short energy payback time, possibility to produce flexible films and high light absorption, which allows producing very thin solar cells. However, current technology has to be improved in order to enhance organic solar cell stability and efficiency, especially in large area production.

In view of the global warming and the increasing importance of environmental protection, it is essential to consider the impact on the environment in implementation of any technology, such as greenhouse gas emissions and energy efficiency. A life cycle analysis is one of the best types of assessment. Such studies of life cycle analysis for organic solar cells are available only recently and few, however, they give an insight into the impact of this technology on the environment. However, it has to be mentioned that the results of life cycle analysis are dependent on solar cell efficiency, life time and solar intensity in location of solar cell.

As one of the key elements of the life cycle analysis is evaluation of energy payback time. Organic photovoltaic energy payback time is estimated to be one of the smallest among renewable energy resources, and it is 0.29 to 0.52 years, which is significantly lower than, for example, in case of biomass (5-10 years), and organic photovoltaic energy payback time is several times smaller than conventional silicon solar cells. Energy payback time comparison of renewable energy sources is shown in Table 1.1.

Another significant environmental impact factor is the greenhouse gas (GHG) emissions. GHG emission level for organic solar cells is significantly lower than silicon solar cells and can be compared with cadmium telluride (CdTe) solar cells. Here it should be mentioned that, in contrast to organic solar cells, in case of CdTe GHG emissions consists primarily of heavy metals because cadmium and telluride are used. GHG emissions can be represented as the CO_2 emission factor. The comparison of CO_2 emission factor for different types of solar cells is shown in Figure 1.1. The efficiency of organic solar elements plays essential role.

Energy payback time EPBT overview of different renewable energy technologies
(D. Yue, et.al., *Energy Environ. Sci.,* 5 (11), p. 9163, 2012.)

Renewable energy technology	EPBT (years)
Biomass combustion	5 – 10
Biomass gasification	<5
Geothermal	0.54
Hydropower	0.5
Amorphous silicon (a-Si) solar cells	1.8 – 3.5
Cadmium telluride (CdTe) solar cells	0.75 – 2.1
Copper indium selenide (CIS) solar cells	1.45 – 2.2
Monocrystalline silicon (mono-Si) solar cells	1.7 – 2.7
Polycrystalline silicon (multi-Si) solar cells	1.5 – 2.6
Organic solar cells (OPV)	0.29 – 0.52
Wind on land	0.26
Wind offshore	0.39

Thus, the advantages of organic solar cells are demonstrated. This type of solar cells can be rated as one of the cleanest sources of energy not only in comparison to fossil fuels, but also compared renewable resources with each other.
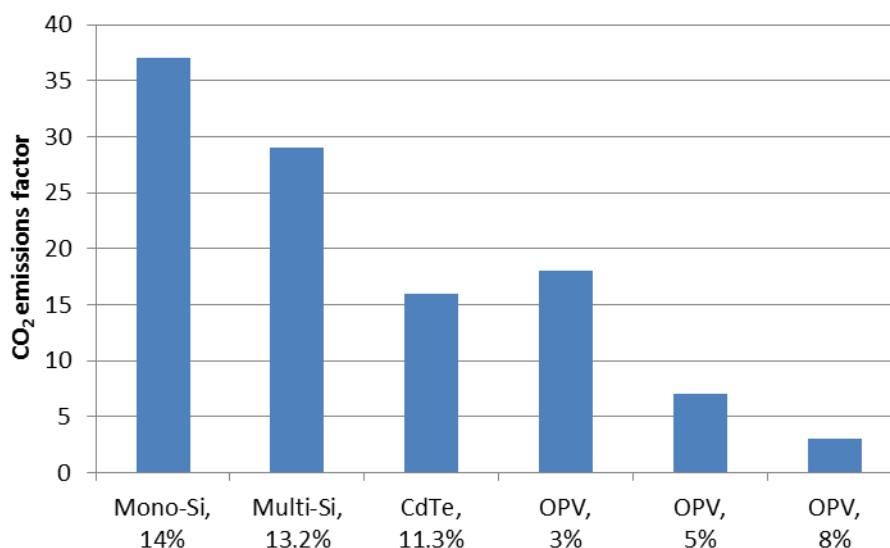

Fig. 1.1. CO_2 emissions factor comparison of different solar cell types: monocrystalline silicon (Mono-Si), polycrystalline silicon (Multi-Si), cadmium telluride (CdTe), organic solar cells (OPV). Power conversion efficiency values of each type of solar cells are given under abbreviations.
(D. Yue, et.al., *Energy Environ. Sci.,* 5 (11), p. 9163, 2012.)

2. EXPERIMENT

2.1. Materials

The derivatives of N,N'-dimetilaminobenziliden-1,3-indandione (DMABI) shown in Figure 2.1 were investigated in this work. DMABI is considered as a promising material for solar cells, because it has good photovoltaic, thermal and chemical properties. Previous studies of DMABI system shows promising applications in organic solar elements. It is also shown that the photoconductivity quantum efficiency β (hυ) for thin films of DMABI molecules is of the order of $1 \cdot 10^{-2}$ el./phot. at 480 nm (~2.6 eV). Photoconductivity threshold energy E_{th} has been evaluated $E_{th} = 1.95 \pm 0.02$ eV. Added various functional groups were selected with the aim to improve the energy parameters and photovoltaic properties. Thus absorption maximum of compounds MeOBI, MeSBI and DMABI-OH is shifted to the blue side of absorption region compared to DMABI. It allows broadening absorption region of solar cell. Adding trityloxyethyl group allows forming thin films of organic material from solution. It can replace polymer and offer lower production costs, better reproducibility of the synthesis, as well as an easier recycling.
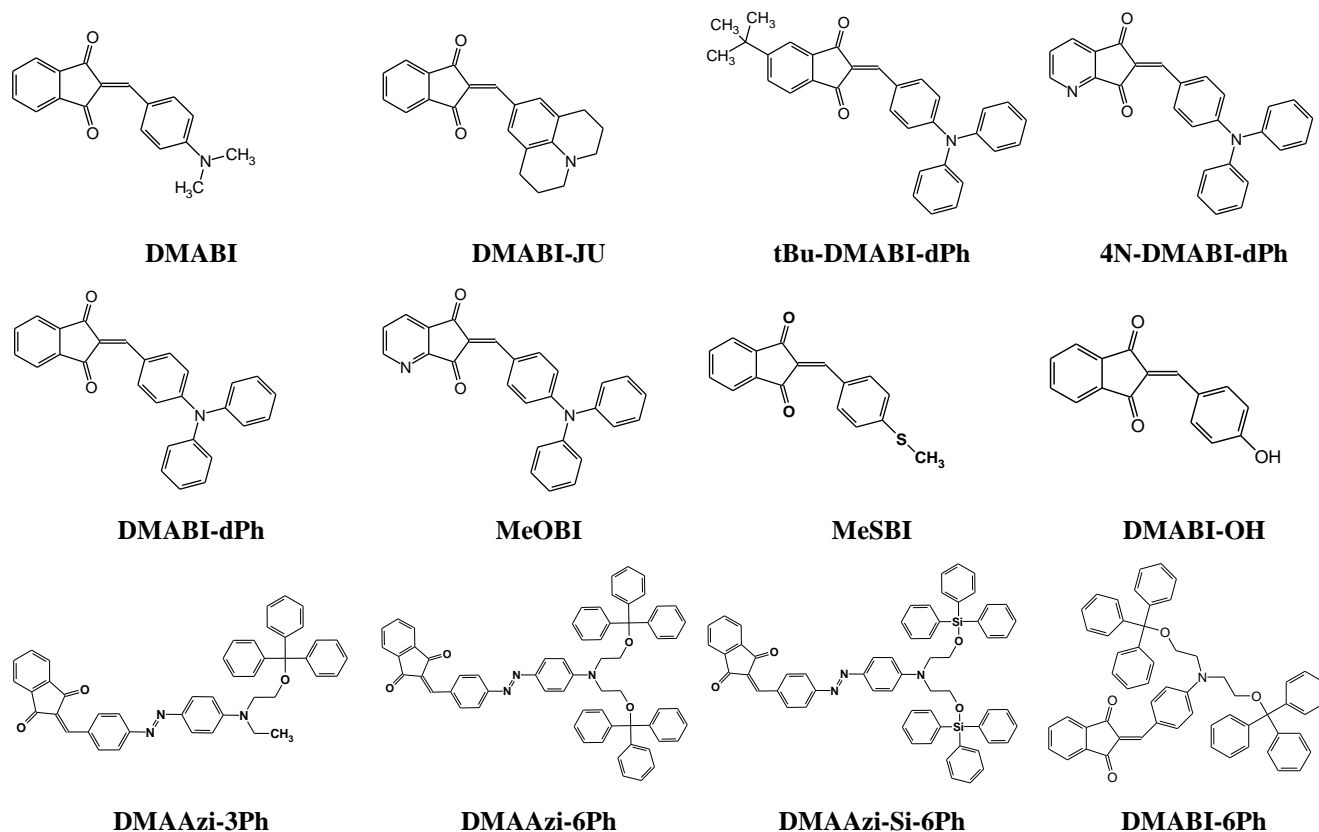

DMABI	**DMABI-JU**	**tBu-DMABI-dPh**	**4N-DMABI-dPh**
DMABI-dPh	**MeOBI**	**MeSBI**	**DMABI-OH**
DMAAzi-3Ph	**DMAAzi-6Ph**	**DMAAzi-Si-6Ph**	**DMABI-6Ph**

Fig. 2.1. Chemical structure of investigated compounds.

2.2. Experimental methods

2.2.1. Sample preparation methods

A series of samples were made to investigate the materials. A thermal evaporation in vacuum and spin coating technique were used to make samples and prototypes. Thin films from solution were made by spin coating technique.

A thermal evaporation in vacuum was used to make multilayer structure and metal electrodes. The system used for thermal evaporation is shown in Figure 2.2. A.
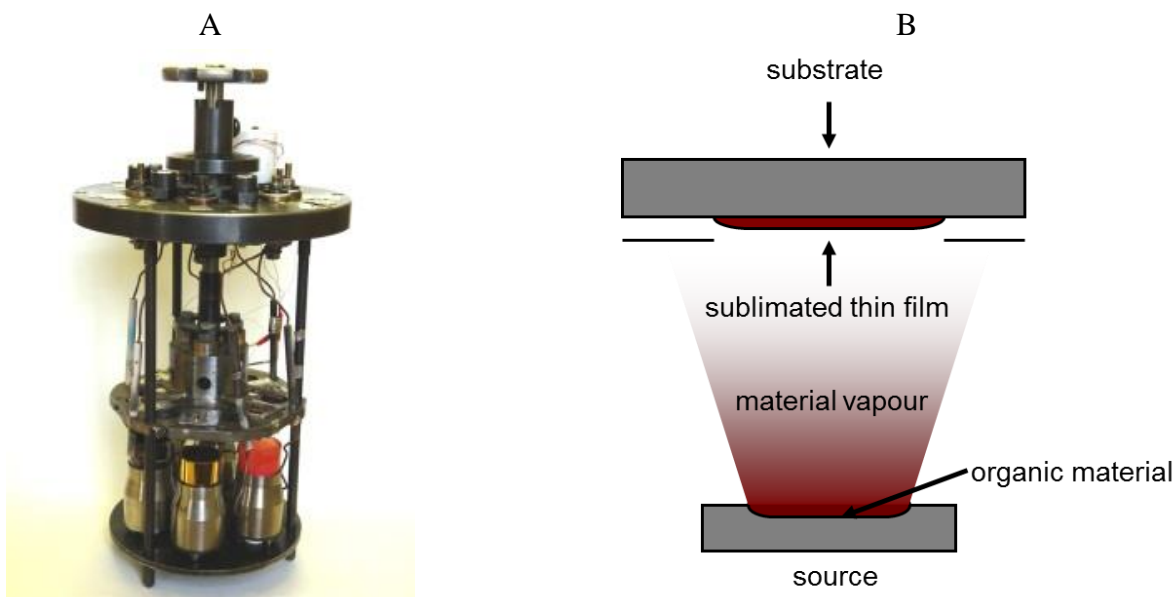

Fig. 2.2. Thermal evaporation in vacuum system (A); schematic process of sublimation (B).

Thermal evaporation in vacuum system consists of three main parts- vacuum chamber, pump system and electronic part. The sublimation process takes part in vacuum chamber – the thin film is formed at necessary level of vacuum. There is a multifunctional stand in chamber that includes the mechanisms to provide sublimation - on the lower level it has six metal boats, filled with materials for evaporation. In the middle level there is a rotatable sample holder. In the upper level there are electrical contacts. They are connected to the boats and supply the electricity to heat materials (Figure 2.2 B). Evaporation process takes place at the vacuum level 10^{-5}-10^{-6} mbar, which is achieved by using a turbomolecular pumping system CDK250.

The commercial thermal evaporation system BOC Edwards - Auto 306 also was used to make several samples. It can be used for preparation of both organic and metal layers. The main advantage of

this device is possibility to determine the film thickness during sublimation and control layer growth rate.

Spin coating system "Laurell" 650 (Figure 2.3 A, B) was used to make samples from solution. The substrate of the sample is fixed on the rotating disk during the process. This is achieved using a vacuum pump. Acceleration and rotation speed can be varied. The rotation speed was changed from 300 to 800 rpm for obtaining different thickness layers.

A typical sample preparation is as follows: ITO covered glass is used as a substrate, it is covered with PEDOT:PSS using a spin coating method (80 seconds at 2500 rpm); PEDOT:PSS layer is dried for 30 minutes at 160°C; organic compound solution is made by using a solvent, usually chloroform; organic film thickness is varied by changing the rotational speed; at the end the film is thermally treated.
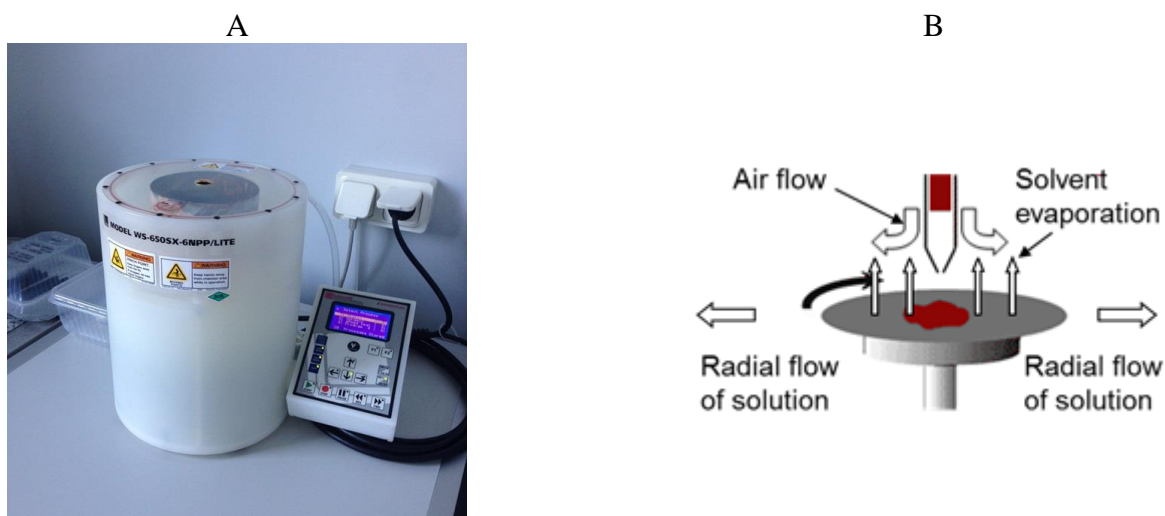
A   B

Fig. 2.3. Spin coating system Laurell 650 (A); schematic process of spin coating method (B).

2.2.2. Characterization of thin films

Quality of thin films after preparing was determined optically. Optical images of thin films were obtained using a high-resolution optical microscope Nikon ECLIPSE L150.

Surface profilometer Dektak 150 was used to determine thickness of the samples. This equipment is designed to determine the sample surface topography.

Absorption spectra of thin films of studied compounds were obtained using a calibrated spectrometer Ocean Optics HR4000.

2.2.3. Photoelectrical measurements

The experimental setup shown in Figure 2.4 was built to study electrical and photoelectrical properties of organic materials. Main part of the setup is a vacuum chamber, combined with a cryostat that provides measurements at different temperatures. All measurements were performed in a vacuum at a pressure of $\sim 6 \cdot 10^{-6}$ mbar.
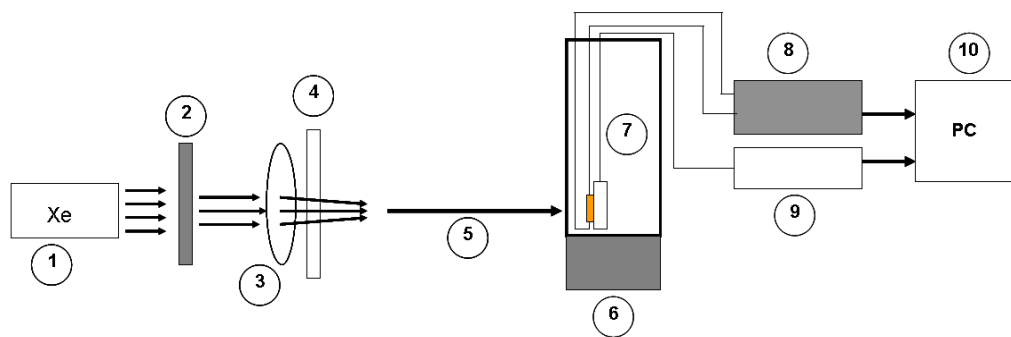

Fig. 2.4. Scheme of experimental setup. 1. Xenon lamp 450W/OFR; 2. Interference filters; 3.Quartz lens 4. Shutter Newport 76993; 5. Optical fiber; 6. Turbomolecular vacuum pump system CDK250; 7. Cryostat; 8. Electrometer Keithley 617; 9. Thermoregulator Lake Shore 332S-T2; 10. Computer.

Before the photoelectrical measurements the current-voltage characteristics were obtained. Photoelectrical measurements consist of current measurement of the alternately illuminated and non illuminated sample. Illumination of the sample was done through quartz glass in a wall of cryostat. The samples were illuminated with a xenon lamp TYP 1450 through interference filters to make spectral measurements of photoconductivity. The spectral region of illumination was selected between 700nm and 300nm, which covers absorption spectra of material. The measurement step was 10 nm. Photocurrent measurements were made at both polarities, illuminated through both – bottom and upper electrodes. Electrometer Keithley 617 with an integrated DC voltage source was used for electrical measurements.

A computer-controlled voltage source and electrometer Keithley 6517 was used to determine the solar cell characteristics. Solar simulator ScienceTech SS150 was used as a light source, which provided a radiation 100mW/cm^2 at AM 1.5 conditions. There were six pixels made on one sample at the same time, each with an active area of 4mm^2. All solar cell measurements were carried out in ambient conditions, without the sample encapsulation.

2.2.4. Formation of energy levels in organic materials

The knowledge of energy levels is of great importance to design efficient multilayer and bulk heterojunction systems of organic materials. A molecule ionization energy of thin film (I_f) and the energy gap has a direct impact on such important processes as photogeneration, separation and transfer

of charge carriers. Knowing these parameters, it is possible to create a material energy diagram. The energy gap is defined as the difference between the hole and the electron transport levels and is called the adiabatic energy gap E_G^{Ad}. It is possible to evaluate it from the threshold energy of photoconductivity E_{th}, which is determined in thin films of low molecular weight organic materials from the spectral dependence of photoconductivity of internal quantum efficiency.

Ionization energy of the molecule, which describes the hole transport level is determined from the photoelectron emission spectrum. Accordingly, the electron affinity level in a thin film (EA_f), which determines the electron transport level, is calculated from threshold energy of photoconductivity and the ionization energy of the molecule.

2.2.5. Characteristics of solar cell

Power conversion efficiency

One of the main characteristics of the solar cell is power conversion efficiency (PCE), which is used to compare solar cells. Efficiency is defined as the ratio of output power from the solar cell and the energy received by the solar element from the sun. Efficiency also depends on the intensity and the spectrum of the light as well as the temperature of the solar cell, therefore measurements should be carried in the constant conditions. As such are taken AM1.5 conditions, 1.5 atmosphere thickness, corresponding to a solar zenith angle of $z = 48.2°$, at a temperature of 25 ° C.

Fill factor

Fill factor (FF) is the second photovoltaic characteristic parameter that determines the relationship between the solar cell maximum possible capacity and actual solar cell capacity.
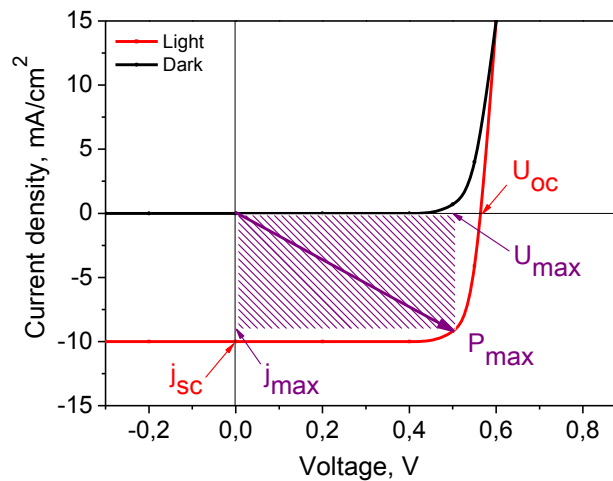
Fig. 2.5. Current-voltage characteristics in the dark and under illumination, where j_{sc} - a short-circuit current density, U_{oc} - an open circuit voltage, j_{max} - current density at maximum power point, U_{max} – voltage at maximum power point, P_{max} - the maximum power that can be obtained from the solar cell.

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FF value can be calculated by obtaining the solar cell current-voltage characteristic when solar cell is under illumination. Fill factor is determined by the ratio between the maximum rectangular area embodied by current-voltage characteristic and rectangular area determined by the j_{sc} and U_{oc} (Figure 2.5). Value j_{sc} is a short-circuit current density. Value U_{oc} is an open circuit voltage. U_{max} – voltage at maximum power point, j_{max} - current density at maximum power point, P_{max} - the maximum power that can be obtained from the solar cell. In a case of ideal solar cell FF reach a value of 1, or 100%. In a case of real organic solar cell FF value is around 0.5 (50%). FF value and shape of current-voltage characteristic also provides information on solar cell quality and the processes that take place in solar cell. If the current-voltage characteristic is obtained as an S-shaped curve with FF <0.25, it means that the solar element has a blocking layer, charge carriers accumulate in it and the mobility of charge carriers is low. S-shaped curve may also indicate a large difference in the electron and hole mobility.

Open circuit voltage

Open circuit voltage U_{oc} is another important characteristic of the solar cell. When solar cell is in the open-circuit voltage mode, the charge carriers generated by electric field is transferred to the electrodes. It provides a potential difference equal to the internal electric field, but directed the opposite. At such a situation the steady-state occurs – generation and recombination of charge carriers are at the same speed and there is no current in a solar cell as a result.

Open circuit voltage is defined by the difference between the higher occupied molecular orbital (HOMO) level of the electron donor material and the lower unoccupied molecular orbital (LUMO) level of the electron acceptor material. HOMO level is related to the molecule ionization energy of thin film I_f and LUMO level is related to the electron affinity level in a thin film EA_f.

Short-circuit current

Short-circuit current flows through the solar cell when the applied voltage is zero - the solar cell is in a short-circuit regime. Short-circuit current is proportional to charge carriers generated under illumination. In a case of ideal solar short-circuit current and the current generated by light is identical, thus short-circuit current is a current at the maximum power point. Short-circuit current depends on several factors: solar cell area, number of photons, spectrum of light, the solar cell absorption and reflection.

3. RESULTS

3.1. Results of classical small molecular compounds

3.1.1. Photocurrent measurements

The samples obtained by thermal evaporation in vacuum method were used in photocurrent measurements. Before detection of photocurrent the current-voltage characteristics were measured to determine the voltage range at which the Ohm's law can be applied - current is linearly depending on voltage. At this stage, the current in the sample is determined only by charge carriers in thermal equilibrium and charge carriers injection from the electrodes do not prevail over charge carriers in thermal equilibrium.

Photocurrent values were measured at different wavelengths light in a spectral region from 300nm to 700nm. This spectral region is close to the solar spectrum energy maximum. Figure 3.1 (A) shows an example of current of one of the highest quality thin films with 4N-DMABI-dPh compound. The current dependence on time was taken, while the sample was alternately illuminated and darkened. From 0 to 100 seconds the sample was in dark. From 100 to 200 seconds the sample was illuminated. Rapid changes of current value were observed and saturated photocurrent was obtained within a few seconds. The photocurrent value was obtained by subtracting the dark current value from the current value at light.
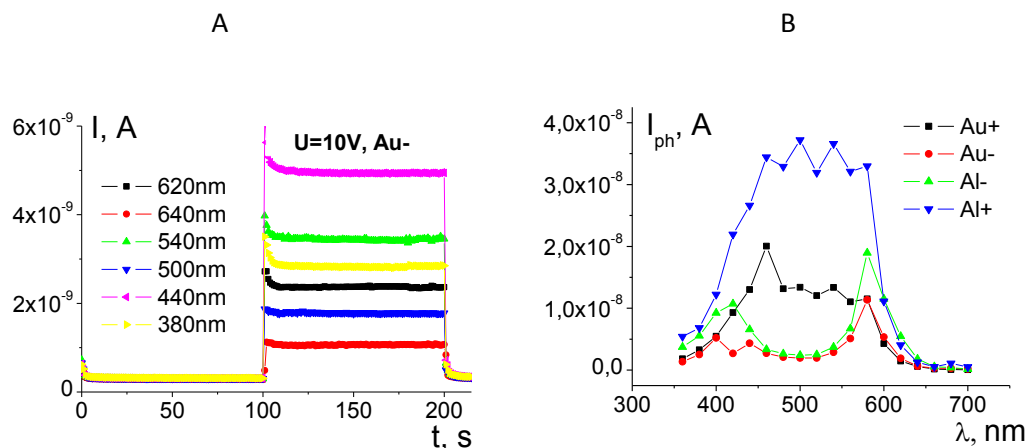
A   B

Fig. 3.1. Current changes of 4N-DMABI-dPh layer under irradiation (A); photocurrent dependence on wavelength (B).

Each sample was irradiated through both electrodes and at both voltage polarities, thus four curves were obtained (Figure 3.1. (B)). Au +, Au- were irradiated through Au electrode, while Al- and Al+ were irradiated through Al electrode.

3.1.2. Energy level determination

Using determined photocurrent values, it is possible to calculate photoconductivity quantum efficiency. Photoconductivity is a material property to become more conductive under influence of electromagnetic radiance. Absorbing photons the photogeneration process occurs in the molecule – photorelease of localized charge carriers, thus allowing them to participate in current conduction process. In order to characterize photoconductivity of material, photoconductivity quantum efficiency β (hν) can be used and is calculated by the formula:

$$\beta(h\nu) = \frac{j_{ph}(h\nu)}{e \cdot k(h\nu) \cdot I(h\nu) \cdot g(h\nu)}, \tag{1}$$

where $j_{ph}(h\nu)$- density of the photocurrent at a given photon energy hν, $k(h\nu)$- transmission of semi-transparent electrode, $I(h\nu)$- intensity of light (phot/cm^{2}s), e- elementary charge, $g(h\nu)$- the coefficient which characterizes absorbed light in organic layer.

From spectral dependence of photoconductivity quantum efficiency is possible to determine energy gap of material as a difference between hole and electron transport levels and is called as adiabatic energy gap E_G^{Ad}. It is possible to calculate it from photoconductivity threshold energy E_{th}, which in its turn is determined from spectral dependence of photoconductivity quantum efficiency. If these parameters are known, energy diagram of material can be created. Knowing energy diagram of material helps to create an effective solar cell.

Graphs of spectral dependence of quantum efficiency in case of 4N-DMABI-dPh are shown in Figure 3.2 A.
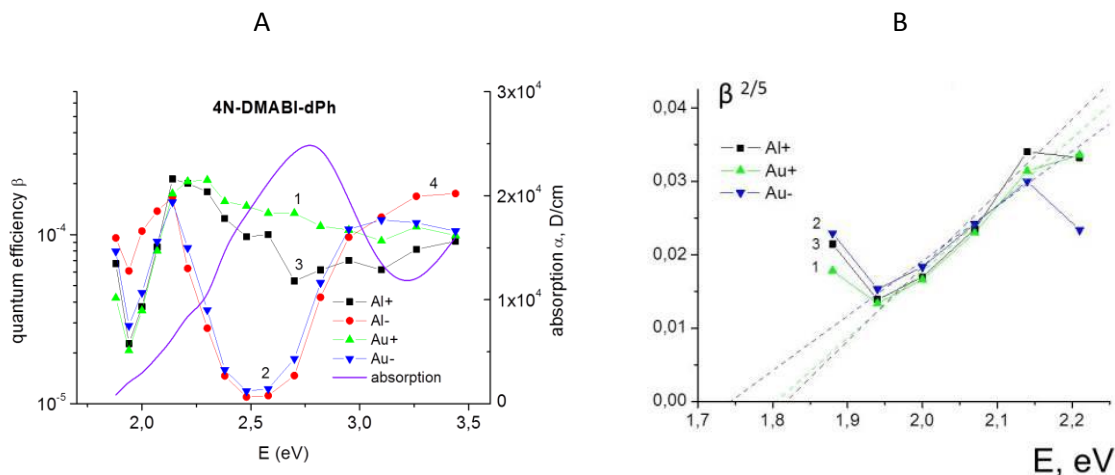

Fig. 3.2. Spectral dependences of photoconductivity quantum efficiency in case of 4N-DMABI-dPh (irradiation through positive Au electrode (1), negative Au electrode (2), positive Al electrode (3) and negative Al electrode (4) at voltage U=10V, the absorption line is also shown in graph) (A); approximation of photoconductivity threshold energy (B).

There should be an anti-correlation between spectral dependence of photoconductivity quantum efficiency and absorption spectrum. Only then it is possible to assume that all measured processes take place in bulk of material, rather than on the surface of the electrodes and the properties of material are measured.

The determination of photoconductivity threshold energy E_{th} is shown in Figure 3.2 B. Previous results demonstrate that in case of anthracene-type crystals spectral dependence of $\beta(h\upsilon)$ in the near-threshold region can be approximated by the equation:

$$\beta(h\upsilon) = A(h\upsilon - E_{th})^n, \tag{2}$$

where $n \approx 5/2$ and E_{th} is photoconductivity threshold energy, A is a coefficient.

Several methods can be used to characterize the energy gap of the organic molecules in the solid state. In case of organic crystals, the charge carriers are not considered as free electrons and holes. They form polaron type quasi-particle included in the electronic and vibronic polarization "clouds". The energy difference between the electronically relaxed hole and electron can be attributed to the optical energy gap $E_G{}^{Opt}$. In order to determine this value the absorption spectrum curve threshold of thin film of organic material at low energies is used.

The experimentally obtained energy value results of sublimed thin films of indandione containing compounds are summarized in Table 3.1. There also shown red-ox potential of investigated compounds in solution which indirectly relates to adiabatic energy gap. In this method energy values are determined from the oxidation and reduction voltage in cyclic voltammetry (determined by Dr. Baiba Turovska- senior researcher at Latvian Institute of Organic Synthesis).

Table 3.1.

The energy level comparison of investigated compounds containing indandione part

	U_{redox}, eV	E_{Th}, eV	$E^G{}_{Opt}$, eV
DMABI	2.25	1.95 ±0.05	-
DMABI-dPh	2.22	1.92 ±0.03	2.05 ±0.04
N-DMABI-dPh	2.09	1.78 ±0.05	1.90 ±0.04
tBu-DMABI-dPh	2.23	1.90 ±0.04	2.20 ±0.05
DMABI-JU	2.12	1.75 ±0.02	2.00 ±0.03
MeOBI	2.87	2.44 ±0.05	-
MeSBI	2.47	2.23 ±0.05	-
DMABI-OH	2.72	2.05 ±0.06	2.62 ±0.06

In case of DMABI, MeOBI and MeSBI, the optical energy gap values could not be determined. Absorption spectra of sublimed films with large scattering influence were obtained and the absorption

threshold value was not detectable. High light-scattering in a layer was due to a significant surface roughness affected by formation of polycrystalline structure in sublimed films.

The conclusions can be made about the studied materials from photoconductivity threshold values given in table 3.1. It is possible to notice that in case of materials DMABI-dPh and 4N-DMABI-dPh photoconductivity threshold value has decreased by ~ 0.14eV. This has happened because carbon atom is replaced by nitrogen atom in 1,3 indandione part. If one compares the DMABI and DMABI-DPH, then here too there has been a decrease of the value as the methyl groups has been replaced by phenyl groups. Photoconductivity threshold energy value in case of DMABI is 1.95eV. In case of DMABI-dPh it has slightly decreased to 1.92eV.

Three compounds MeOBI, MeSBI and DMABI-OH aroused particular attention, which threshold energy values were obtained significantly higher than other compounds. The increase of energy gap in material is connected with solar cell efficiency. One of the values that influence the efficiency is open circuit voltage. Energy gap of material is the difference between the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level. In two-material system open circuit voltage is mainly determined by the difference between the HOMO level of the donor material and LUMO level of acceptor material. The use of studied materials in combination with materials of similar HOMO and LUMO energy levels and wide energy gap could increase solar cell efficiency.

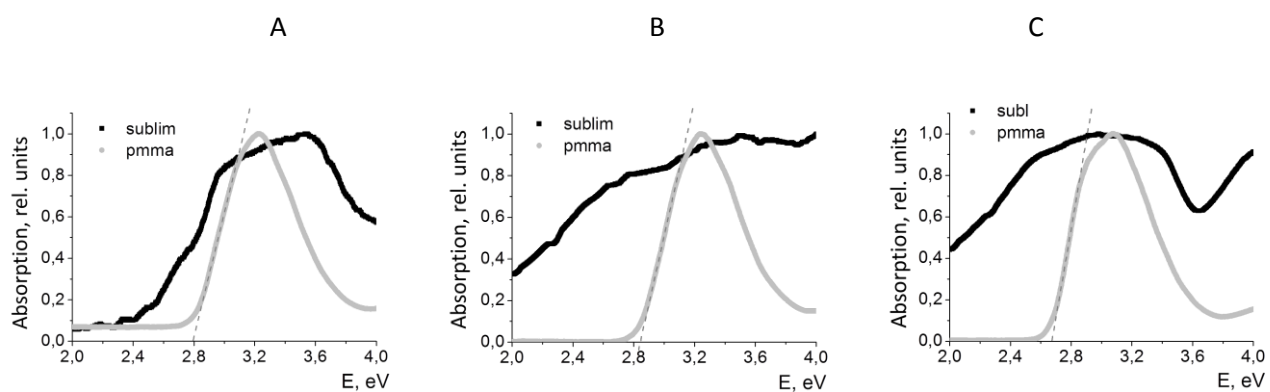The absorption spectra of MeOBI, MeSBI and DMABI-OH are shown in Figure 3.3 A, B, C.

Fig. 3.3. Absorption spectra of DMABI-OH (A), MeOBI (B), MeSBI (C) sublimed and spin-coated samples (in PMMA matrix). Optical band gap is determined from absorption spectra for spin-coated samples.

As previously mentioned, the absorption spectra for these materials were obtained broad and the absorption maximum was difficult to determine. To avoid this, materials MeOBI, MeSBI and DMABI-OH were mixed into the polymer polymethyl methacrylate (PMMA) matrix and thin films for absorption determination were made from solution. Absorption maxima obtained from guest-host films

were from 3.1 to 3.3 eV. When compared with pure DMABI which absorption maximum is at 2.6eV, the absorption peaks of the studied compounds is shifted to the ultraviolet region of the spectrum.

Evaporated film absorption spectra could not be used also for determination of the optical energy gap. Therefore, these values were obtained from spin-coated samples where organic material was mixed in the PMMA matrix (Figure 3.4). The higher values were obtained for MeOBI film, E_G^{Opt}=2.85±0.03eV. Optical energy gap values for DMABI-OH and MeSBI films were obtained E_G^{Opt}=2.80±0.03eV and E_G^{Opt}=2.68±0.03eV, respectively. As previously mentioned, broadening the absorption spectra of solar cell by using materials with different light absorption spectra is one of the possibilities to increase the efficiency of organic solar cell.
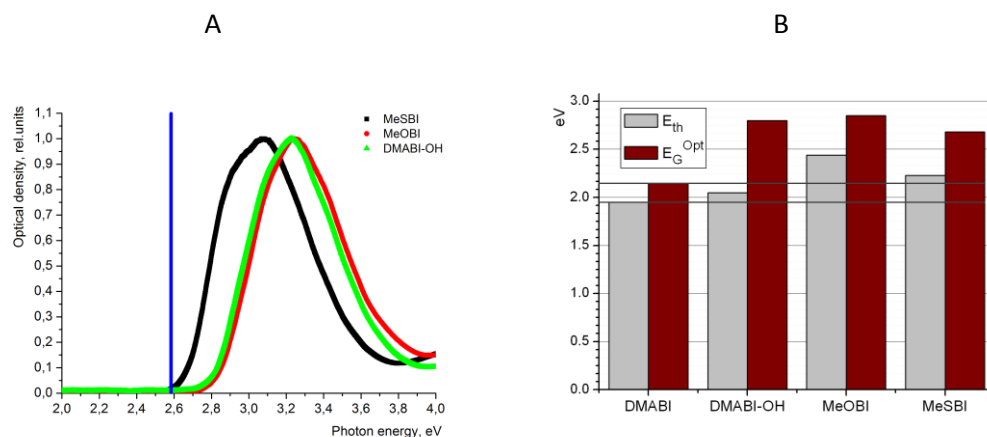

Fig. 3.4. Comparison of absorption spectra of investigated materials with DMABI (spin-coated samples). The blue line corresponds to the absorption maximum of DMABI) (A); threshold energy of photoconductivity E_{th} and optical energy gap E_G^{Opt} values of MeOBI, MeSBI and DMABi-OH compared with values of DMABI (B).

Figure 3.4 A shows the comparison of absorption spectra. The blue line marks pure DMABI absorption maximum. Such absorption spectra values of studied compounds allow using them in tandem solar cells. The studied compounds are capable of absorbing ultraviolet light and let through the red light contrary, for example, silicon. Such a combination of several materials with different light absorption region gives the possibility to use a higher proportion of sunlight.

It was also compared photoconductivity spectral dependence of quantum efficiency β(hυ) on irradiation through Au and Al electrodes at both polarities for MeOBI, MeSBI and DMABI-OH. Quantum efficiency β(hυ) spectrum character for these compounds was relatively independent of the electrode polarity and the case which electrode is irradiated (Figure 3.5). Compared with the absorption spectra, in case of DMABI-OH two absorption peaks were observed in both the long and short wavelength regions.

Anti-correlation between β(hυ) and absorption curves corresponds to the case in which photogeneration process takes place in bulk of organic layer instead of the surface between the

electrode and the organic layer. In case of negative Au electrode values of β(hυ) for DMABI-OH were about one order higher than in the case of a positive Au electrode. This could be due to influence of charge carriers, as β(hυ) is affected not only by photogeneration but also by transport of charge carriers. In case of MeOBI and MeSBI the difference between β(hυ) spectra character depending on the polarity of the electrodes and the irradiation was not explicit (Figure 3.5 B, C). This points to a possible equal electron and hole transfer in these compounds. In case of organic solar cells, such a characteristic is positive, because most materials that are used in such cells are electron transfer materials or hole transfer materials.
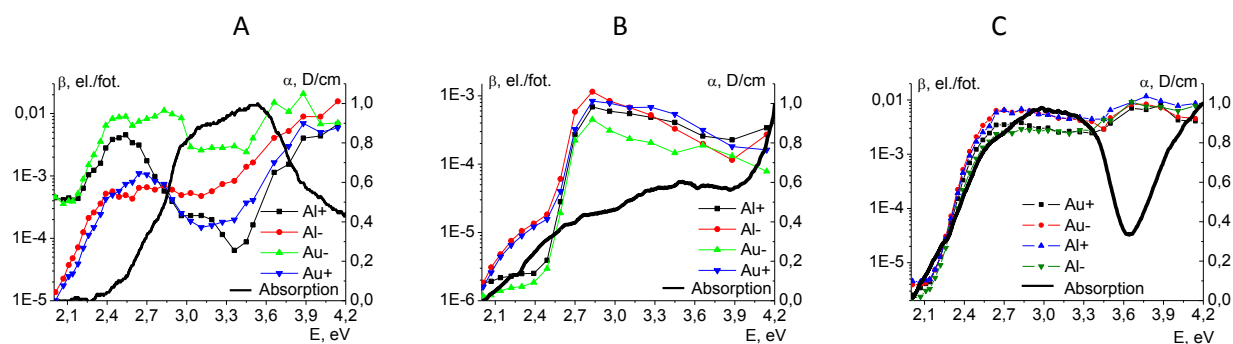

Fig. 3.5. Spectral dependences of quantum efficiency of photoconductivity β(hυ) and absorption spectra of DMABI-OH (A), MeOBI (B), MeSBI (C).

The highest values of β(hυ) were obtained for DMABI-OH and MeSBI and reached $1 \cdot 10^{-2}$ el./phot. at plateau region with photon energy 2.4 to 3.0eV for DMABI-OH and at 3.8eV for MeSBI (Figure 3.5 A). In case of MeSBI this is a maximum point and β(hυ) values are close to $1 \cdot 10^{-2}$ el./phot. at all plateau region from 2.5 to 4.0eV (Figure 3.5 C). These values repeat high values for DMABI acquired previously. The lowest maximum values of β(hυ) were obtained for MeOBI and were $1.15 \cdot 10^{-3}$ el./phot. at 2.8eV (440nm) (Figure 3.5 A).

Photoconductivity threshold energy values E_{th} were determined using equation (2). Photoconductivity threshold energy value for DMABI-OH was obtained E_{th}=2.05±0.03eV, for MeOBI E_{th}=2.44±0.03eV and for MeSBI E_{th}=2.23±0.03eV.

Determination of organic material energy gap value plays an important role in creation of solar cell. If more than one material is used, it is necessary to know the compatibility of them. Determined energy level values give information on the location of the studied compound in energy diagram. Both E_{th} and E_G^{Opt} values for studied materials are greater than for pure DMABI (E_{th}= 1.95±0.02 and E_G^{Opt}=2.15±0.03). The comparison of these values is shown in Figure 3.4 B. The increase of energy gap means that these compounds will absorb light closer to ultraviolet spectral region, but the width of

absorption spectrum will be narrower. Such characteristics allow using these materials in tandem solar cells in combination with other compounds.

3.1.3. Solar cell prototypes

Taking into account the results and energy level values obtained in previous chapter the most suitable materials were selected for further study in solar cells. Each of the materials used in the study has different characteristics that make it as more suitable in different type of solar cells. Prototypes were created for three widely used organic solar cell types: dye-sensitized solar cell, layered structure and bulk heterojunction, which includes both the use of the polymer and the polymer substitution with low molecular weight compounds.

Results for dye-sensitized solar cells

The organic material in dye-sensitized solar cells is used as a dye that fills the base substance TiO_2 porous layer. DMABI (N,N'-dimetilaminobenziliden-1,3indandione) was chosen as the most perspective studied materials for this type of solar cells because its photocurrent showed high values. To create dye-sensitized solar cell an electrolyte is of great importance, but electrolyte is also problematic as it is used in a liquid form. This makes it difficult to provide a long life time of solar cell due to encapsulation.

The results of dye-sensitized solar cells are summarized in table 3.2.

Table 3.2.

Solar cell characteristics for dye-sensitized solar cells

Sample	j_{sc}, mA/cm2	U_{oc}, V	PCE, %	FF
DMABI	0,0097±0,0005	0,22±0,01	7,1E-04±0,35E-04	0,34±0,02

The power conversion efficiency (PCE) for this type of solar element is very low. The fill factor is better, while the open circuit voltage is low. As one of the main factors affecting the low efficiency is DMABI crystallization already at the beginning of TiO_2 pore filling. As a result the pores are blocked, and only a small part of TiO_2 layer is filled with organic material. The other reason of low efficiency could be explained by the lack of encapsulation. The rapid fall of efficiency was observed as electrolyte became dry.

Results for layered structure solar cells

As the most perspective material for layered structure solar cells was chosen 4N-DMABI-dPh (4N(4N',N'-diphenylamino-benziliden)indan-1,3dione) in combination with DMABI. 4N-DMABI-dPh was chosen as it forms sublimed thin films with one of the best quality. The good quality film is necessary to create an efficient layered structure solar cell. DMABI was chosen as it has high photocurrent values. The obtained results are shown in table 3.3.

Table 3.3.

Solar cell characteristics for layered structure solar cells

Sample	j_{sc}, mA/cm2	U_{oc}, V	PCE, %	FF
Au/DMABI/4N-DMABI-dPh/Al	0,0002±1E-5	0,73±0,04	3,2E-05±0,1-05	0,21±0,01

The obtained results show low power conversion efficiency. This could be explained due to several factors. Efficiency for layered structure solar cells are low in general, because the active area is located just in the interface of two layers and solar cell, although it was made in a vacuum, after preparation came into contact with oxygen as it was not possible to ensure location of measuring equipment in a vacuum or in a neutral atmosphere. Influence of oxygen stimulates formation of defects in organic material, which result in a trap level formation. They, in turn, block charge carrier transfer and reduce current.

The fill factor FF is also low for this type of system. It is influenced by thin film quality. The open circuit voltage shoes good results. The values are relatively high. Usually it is around the value of 0.5V for organic solar cells. This means that materials were selected properly. As it was mentioned in chapter 1.3., the open circuit voltage is also determined by the substances used, not only by solar cell quality - the open circuit voltage is determined by the difference between the electron HOMO level of electron donor material and LUMO level of electron acceptor material.

Results for bulk heterojunction solar cells

The most suitable material for bulk heterojunction was also selected DMABI because of its high photoeffect. To prepare bulk heterojunction solar cell two materials usually are mixed in solution. One of material is an electron acceptor, while the other is an electron donor. In the widely used system P3HT:PCBM polymer P3HT is the donor material, but PCBM is the acceptor material.

Since DMABI, as well as other previously analyzed materials are low molecular weight compounds, which do not form thin films from the solution, it was mixed with the polymer P3HT,

because this is only way to obtain high-quality thin films. The system DMABI: P3HT was prepared. Power conversion efficiency 0.001% was obtained for such system. Compared to the other types of solar cells, there has been no improvement in efficiency, although theoretically it is believed that indandione containing compounds would be best applicable in bulk heterojunction solar cells, however, the obtained efficiency is low and the possible application is difficult. The main reason for low efficiency is incompatibility of the two materials used. As mentioned above, the solar element must consist of donor and acceptor material, but good quality film can be obtained only by using a polymer P3HT, which is the donor material. Indandione-containing compounds also can be evaluated as a donor material. In the solar cell formed of two materials both electron donor materials charge carrier transfer is difficult, thus also the efficiency is low. To solve this problem, indandione containing low molecular weight materials which form amorphous (glass structure) thin films would be necessary, so they can be combined with PCBM.

3.1.4. Improvement of organic solar cells efficiency

Another application of the studied materials was examined their use for power conversion efficiency improvement of already known systems. It would be possible by adding the compound to the system as admixture. Good characteristics for such prospective application showed studied compound MeSBI (2-(4-methylsulfanyl-benzylidene)-indan-1,3-dione) due to its absorption spectrum.

One of the best results by now in the formation of organic solar cells is achieved using regioregular polyheksyltiohpene (P3HT) as the electron donor, together with the fullerene derivative PCBM as the electron acceptor. One of the weaknesses of such systems is the lack of spectral range (350-650nm), furthermore a decrease in absorbance at 400 nm region for such a system is observed.
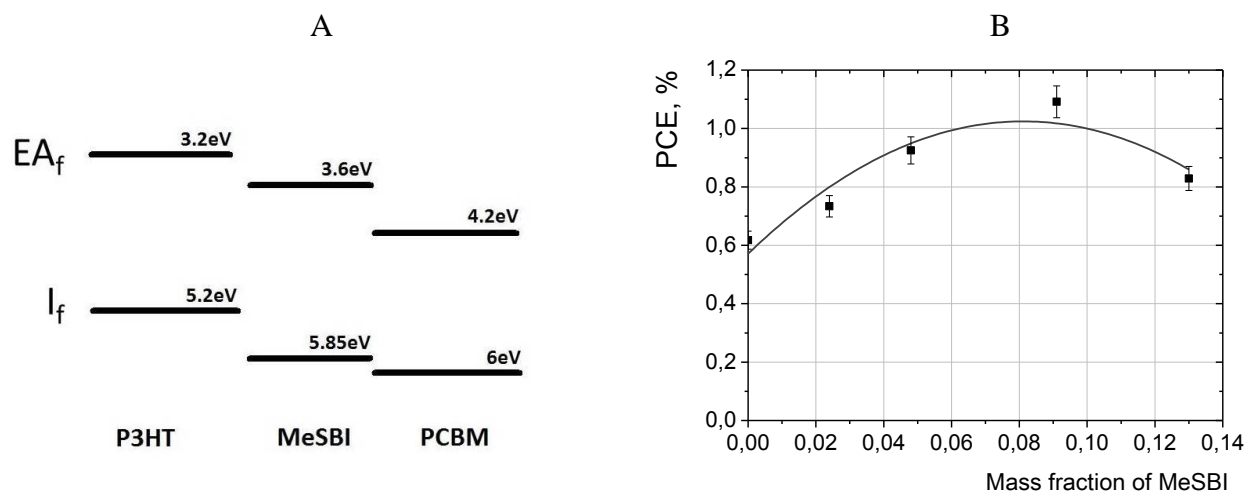

Fig. 3.6. Energy level diagram for materials used in solar cell system P3HT:MeSBI:PCBM – polymer P3HT, studied compound MeSBI, fullerene derivative PCBM (A); Power conversion efficiency PCE dependence on mass fraction of MeSBI in solar cell system P3HT:MeSBI:PCBM (B)

Absorption maximum for studied indandione derivative MeSBI is directly at 400 nm, thus it would be possible to increase the amount of light absorbed by used system P3HT:PCBM by addition of indandione derivative MeSBI in this system.

Distribution of MeSBI energy levels also showed perspective properties. Both the molecular ionization energy value of thin films I_f that correlate with the highest occupied molecular orbital HOMO level and the values of electron affinity level of a thin film of EA_f, which correlates with the lowest unoccupied molecular orbital LUMO level, for this compound was between the values of P3HT and PCBM. This means that MeSBI adding to P3HT:PCBM system assist charge transfer between P3HT and PCBM. The distribution of energy levels is shown in Figure 3.6 A.

Adding MeSBI significantly improved the P3HT: PCBM system power conversion efficiency PCE raising it from 0.6% (without MeSBI) to 1.1% (mass fraction MeSBI 0:09). Power conversion efficiency dependence on added MeSBI mass fraction is shown in Figure 3.7 B. The calculations were made and the equation $y = -66,95x^2 + 11,18x + 0,57$ was obtained, which describes the power conversion efficiency dependence on mass fraction of MeSBI in the system was obtained. The correlation coefficient value of 0.95 was obtained for equation, which means that this equation can be used to calculate the best possible power conversion efficiency of such system. At the given conditions the maximum value is very close to the experimental value.

Although the acquired power conversion efficiency is less than the best reported in literature, for this type of systems, however, it is comparable. It should be emphasized that solar cells used in this work were made in the air at the room atmosphere and were not encapsulated. Oxygen access to the solar cell significantly reduces its efficiency. In this case, attention should be paid to the change of power conversion efficiency rather than absolute values.

The results of MeSBI are considered as a promising for commercialization and the results have been submitted for patent (patent application No. P-14-24).

3.2. Results of glass structure forming small molecular compounds

In cooperation with chemists of Riga Technical University Material Science and Applied Chemistry faculty for the first time indandione containing low molecular weight compounds that form glass structure layer of solution were synthesized. Accordingly, it allows to build solar cells which consist only of low molecular weight compounds and to make them from solution. The traditional method for manufacturing thin films - vacuum thermal deposition is costly and requires large amounts

of energy. Thin films fabrication of solution saves energy and raw materials, particularly when printing or "roll-to-roll" method applied.

Fabrication of solution using low molecular weight materials instead of polymer is attractive also because repeatability of low molecular weight compounds synthesis is significantly higher than synthesis of polymers, while the recycling process is much easier. Likewise, if the compound has a large absorption in the visible part of the spectrum, photovoltaic applications of such compound is promising. Indandione fragment containing azobenzene compounds with attached tri-phenyl groups are one of such low molecular weight compounds which have both high absorption coefficient and also they form amorphous structures from solution. Thus, these materials can be applied to the creation of innovative solar cells, reducing production costs and allowing building them flexible and small size which extends the application.

3.2.1. Energy level determination

In this work four original organic glass structure forming compounds containing indandione and azobenzene groups were investigated: 2-(4-(4-N-ethyl, N-tritylethylamino)-phenyl-diazylidene)-benzylidene-indene-1,3-dione (DMAAzi-3Ph), 2-(4-((4-(Bis(2(trityloxy) ethyl) amino) phenyl)diazenyl) benzylidene)-1H-indene-1,3(2H)-dione (DMAAzi-6Ph), 2-(4-(4-N,N-di-triphenyl sililoxyethyl- amino)-phenyl-diazilidene)-benzylidene-indene-1,3-dione (DMAAzi-Si-6Ph) and 2-[[4-(bis(2-trityloxyethyl)amino)phenyl]methylene]indane-1,3-dione (DMABI-6Ph).

The structural formulas of these compounds are shown in Figure 2.1. Different tri-phenyl groups are attached to compounds to help forming amorphous thin film from solution. Compounds DMAAzi-3Ph and DMAAzi-6Ph have carbon between the phenyl rings. This structure is stronger than DMAAzi-Si-6Ph, which has silicon between the phenyl rings.
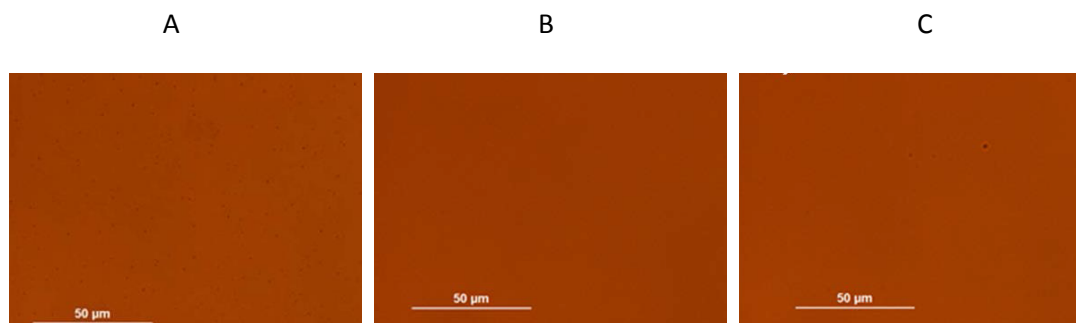

Fig. 3.7. High resolution optical images of DMAAzi-3Ph (A), DMAAzi-6Ph (B), DMAAzi-Si-6Ph (C). Scale of images 50μm.

Optical images give information on the morphology of thin films. Figure 3.7 shows that all the films are amorphous and their optical quality is good. DMMAzi-3Ph layer has some crystals, but their impact on photovoltaic measurements is not significant. Such crystal formation is due to undissolved particles in the solution of high concentrations.
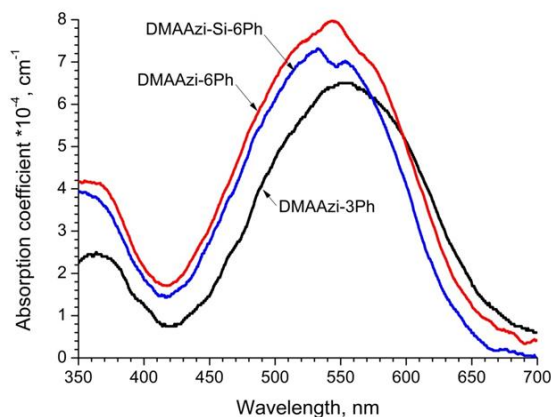

Fig. 3.8. Absorption spectra of DMAAzi-3Ph, DMAAzi-6Ph and DMAAzi-Si-6Ph.

Absorption spectra of investigated compounds DMAAzi-3Ph, DMAAzi-6Ph and DMAAzi-Si-6Ph cover the region of visible spectrum. Absorption spectra of DMAAzi-Si-6Ph and DMAAzi-6Ph are similar but spectrum of DMAAzi-3Ph is shifted to the red side. Absorption is connected with electron transfer in molecule. Added bulky groups should not directly influence electron transfer in molecule as they have no covalent bond. It means that the observed shift to red side can be explained with influence of molecule surroundings. Absorption coefficient maximum reaches 65000 cm^{-1} for thin film of DMAAzi-3Ph, 79700 cm^{-1} for thin film of DMAAzi-6Ph and 73100 cm^{-1} for thin film of DMAAzi-Si-6Ph (Figure 3.8.).
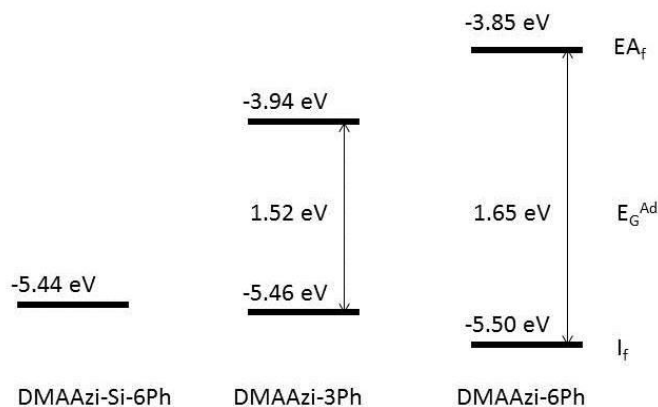

Fig. 3.9. Diagram of energy levels; Upper levels correspond to level of electron affinity in thin films EA_f. Lower levels correspond to molecule ionization energy level in thin films I_f. Values between levels correspond to photoconductivity threshold energy E_{Th}.

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Figure 3.9. shows energy levels of DMAAzi-3Ph, DMAAzi-6Ph and DMAAzi-Si-6Ph. Molecule ionization energy decrease for DMAAzi-Si-6Ph, DMAAzi-3Ph and DMAAzi-6Ph from -5.44±0.03eV to -5.50±0.03eV, respectively.

Molecule ionization energy is level of the molecular polaron and it depends on the electron polarization of the surrounding molecules. Previous studies have shown that trityloksyethyl group is more rigid as triphenylsilyl groups. Silicon forms longer bonds, accordingly bulky group has no explicit one conformation because there are possible bigger C_{Ph2}–C_{Ph1}–Si–O twist angle displacement from stable state as C_{Ph2}–C_{Ph1}–C–O. This means that the distance between the molecules in case of DMAAzi-Si-6Ph could be shorter than in case of DMAAzi-3Ph. DMAAzi-3Ph consists only of one trityloksyethyl group unlike DMAAzi-6Ph. Thus DMAAzi-3Ph molecules are closer than DMAAzi-6Ph molecules. It repeats the sequence of molecular ionization energies and is considered as a major reason for the different ionization energy values.

This also explains different values of the electron affinity levels.

The absorption spectra of studied compounds cover the same region as one of the most widely used polymer for organic solar cells – poly(3-hexylthiophene) (P3HT). It also shows the potential of the studied materials for creation of organic solar cells. P3HT is mostly used with phenyl-C61-butyric acid methyl ester (PCBM) molecules which molecular ionization energy is about -6.2eV and electron affinity -4.0eV. By using studied compounds in combination with PCBM is possible to achieve difference of affinity levels of 0.15eV compared to ~ 1eV in case of P3HT: PCBM system.

3.2.2. Solar cell prototypes

As the best compound for creation of solar cell DMAAzi-3Ph was selected, as the largest photocurrent was observed in it. However, the power conversion efficiency of such a system was obtained PCE = 0.006%, which is considered a low efficiency value.

To improve the results studies of compound DMABI-6Ph were started, because DMABI-6Ph combines good qualities of DMABI with the ability to form a glass structure thin layer. Two-material system was used to make a bulk heterojunction film in solar cell - widely known electron acceptor and transfer material – fullerene derivative [6,6]-phenyl C61-butyric acid methylester (PCBM) and the newly synthesized DMABI-6Ph.
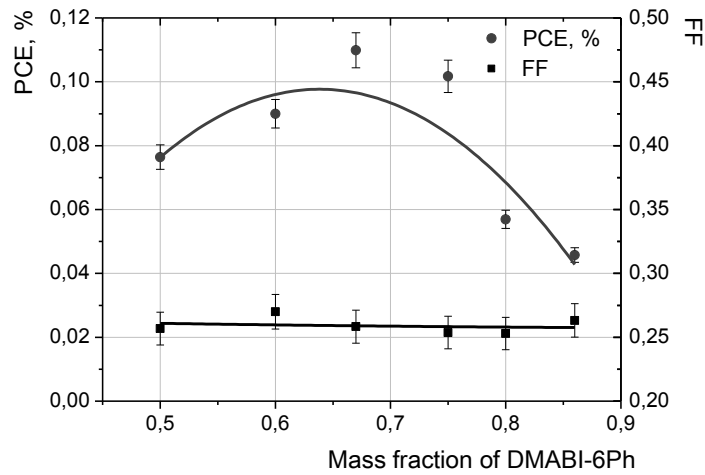
Fig. 3.10. Power conversion efficiency dependence on mass fraction of DMABI-6Ph in system   DMABI-6Ph:PCBM.

Several samples were made with different thicknesses and different mass fraction of DMABI-6Ph in the system. The best power conversion efficiency (PCE) was obtained for the sample with a thickness of 120nm and mass fraction of DMABI-6Ph in the system 0.67, reaching a value of PCE 0.11. Comparing the samples with different mass fraction of DMABI-6Ph in the system, it was observed that the biggest efficiency values are achievable when mass fraction of DMABI-6Ph in the system is in the range of 0.60 to 0.75. In the same time the fill factor FF values remain nearly constant at about 0.26 (Figure 3.10). After calculations the equation that describes the power conversion efficiency PCE was obtained: $y = -1.52x^2 + 1.97x - 0.53$. Equation was obtained with correlation coefficient value 0.94, which means that this equation is possible to use for calculation of the best possible power conversion efficiency. At the given conditions the maximum value is very close to the experimental value.
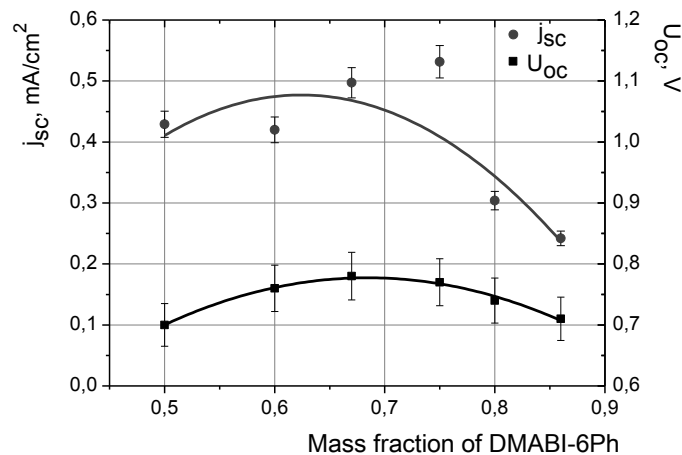

Fig. 3.11. Short circuit current density j_{SC} and open circuit voltage U_{OC} dependence on mass fraction of DMABI-6Ph in solar cell system DMABI-6Ph:PCBM.

Figure 3.11 shows the values of solar cell characteristics short circuit current density j_{sc} and open circuit voltage U_{oc}. The graph shows that the efficiency increase is mainly determined by the short circuit current and open circuit voltage. The best of the open circuit voltage value was observed at mass fraction 0.67 and reaches the $U_{OC} = 0.76V$. This value is considerably higher than the value which has been previously obtained for indandione containing glass structure forming compounds ZWK-1TB. It had $U_{OC} = 0.17$ and it was obtained by sample illumination at one particular wavelength of 490nm instead of full solar spectrum. Similarly, the current values are obtained significantly higher. Best value reached $I_{sc}=0.53$ mA/cm^2, while in the case of ZWK-1TB short circuit current value was only 0.076 mA/cm^2. There is a rapid decrease in current when mass fraction reaches the value of 0.80. This agrees with a significant drop in efficiency. It allows suggesting that the key factor of studied solar cells efficiency changes has been directly short circuit current.

The obtained value of open circuit voltage for system DMABI-6Ph:PCBM was also higher than for one of the best organic photovoltaic systems using polymer P3HT and low molecular weight compound PCBM. Open circuit voltage value for such a system reaches about 0.6V. This means that the studied compounds are promising as is directly affected by used materials. As previously mentioned open circuit voltage is determined by the difference between the highest occupied molecular level of donor material and the lowest unoccupied molecular level of acceptor material.

The least influence of studied compounds different concentration was observed in case of fill factor FF (Figure 3.10). The FF value for all studied samples is around 0.26 which is assessed as low. Average FF values for polymer solar cells P3HT:PCBM reache around 0.5. Low FF values are evaluated as one of the reasons why the efficiency values are below 1% level. FF value 0.26 shows that there were problems with charge carrier mobility in the investigated samples. In case of DMABI-6Ph charge carrier mobility is dispersed throughout the sample, which significantly reduces charge carrier transport to the electrodes. Such problems can be avoided by modifying the compound DMABI-6Ph with other functional groups that could improve charge carrier mobility. Another option to improve FF values is to add an additional electron and hole transport layers in the system.

The obtained solar cell efficiency values are comparable to some of the values of widely used polymer systems reaching 1% power conversion efficiency, however, obtained power conversion efficiency values for studied compounds are less than the best-known P3HT:PCBM efficiency values. Best PCE values for polymer solar cells reache 3-6%. As previously mentioned, one of the reasons is the low value of FF. It should be also taken into account that the samples were made and all the photoelectric measurements were performed at ambient conditions in the air and samples were not

encapsulated. That significantly reduces the efficiency. Better results would be expected if the production of samples and measuring takes place in the vacuum or inert atmosphere but it was not possible due to equipment. Encapsulation is of great importance to the solar cell efficiency and lifetime. It prevents samples from influence of oxygen and environmental effects. Performing studies of DMABI-6Ph emphasis was on the solar cell characteristics dependency determination on mass fraction of DMABI-6Ph in the system and therefore multilayer system was not designed and less attention was paid to the delimitation of the solar cell from the environment influence.

Since charge carrier transfer dispersion through the sample was observed for DMABI-6Ph, it is possible to improve efficiency by modifying molecules with other functional groups that improve charge carrier transport, for example, using the carbazole functional groups.

CONCLUSIONS

1. Indandione containing material class has been defined as the potentially perspective for organic solar cells.

2. The relation between energy values of the studied materials has been obtained. It allows to judge about the photovoltaic properties of each material thus enabling to choose the most promising materials without time-consuming experiments.

3. The most promising materials for layered structure, dye sensitized and bulk heterojunction solar cells have been determined and the prototypes have been made.

4. It has been found shown that material MeSBI increases power conversion efficiency of widely used organic solar cell system P3HT: PCBM from 0.6% without MeSBI to 1.1% with MeSBI.

5. Three materials MeOBI, MeSBI and DMABI-OH can be applied in tandem solar cells, broadening the absorption spectrum of the solar cell. Compared with the pure DMABI, studied materials have a wider energy gap - higher energy threshold at an early stage of absorption. This feature allows using the compounds in creation of tandem solar cell. The shift of absorption spectrum of studied materials gives the possibility to extend the organic solar cell spectral region of light absorption, combining them with other materials, with different absorption.

6. The largest power conversion efficiency has been obtained for bulk heterojunction solar cells. Four newly synthesized innovative materials DMAAzi-3Ph, DMAAzi-6Ph, DMAAzi-Si-6Ph and DMABI-6Ph were studied which are capable of forming glass structure thin films from solution. This was achieved by adding tri-phenyl groups to molecules. Thin film made of the

solution is smooth, and reduce manufacturing costs, since there is no need for large amount of energy as in case of thermal sublimation. These compounds have similar absorption spectra to a widely used polymer P3HT It is in the visible region with a high absorption coefficient up to 79700 cm[1].

7. Energy levels and solar cell characteristics have been determined for studied materials DMAAzi-3Ph, DMAAzi-6Ph, DMAAzi-Si-6Ph and DMABI-6Ph. Molecule ionization levels were obtained about -5.45±0.03eV and electron affinity levels of the compounds were obtained about -3.80±0.03eV, thus the electron affinity level was obtained only about 0.15eV below the electron affinity level of PCBM. This is several times less compared to ~1eV for P3HT:PCBM system. These glass structure forming materials have been evaluated as promising component for active layer of solar cells to form a heterojunction with PCBM molecules.

8. The highest power conversion efficiency of glass structure forming materials have been obtained for DMABI-6Ph and reached 0.11%. It can be improved by modifying the molecule to get better charge carrier transport, as well as preparing solar cells in an inert atmosphere and ensuring their encapsulation. Relatively high open circuit voltage value allows assuming that DMABI-6Ph in combination with widely used fullerenes derivative PCBM is a perspective system for organic solar cells.

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