Photovoltaic properties of glass forming pyraniliden derivatives in thin films

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Abstract. Organic solar cells based on solution processable materials could provide new low cost production method. Most popular materials are polymer P3HT and fullerene derivative PCBM. There is active study to find effective low molecular weight materials. Instead of planar structure, most of the research is made on bulk heterojunction samples as they are providing better efficiency. In our work we have studied three newly synthesized materials consisting 2-tert-butyl-6-methyl-4H-pyran-4-ylidene fragment. Each compound has different electron acceptor group. From photoconductivity experiments its threshold values were obtained. For photovoltaic experiments bulk heterojunction samples containing investigated compounds mixed with PCBM were made. Best results with Incident Photon to Charge Carrier Efficiency (IPCE) larger than 0.4% at wavelength between 390 and 570 nm were obtained for system containing compound with malononitrile as electron acceptor group. Still, efficiency could be greatly improved as IPCE spectral dependence is not repeating absorption spectrum which show that generated charge carriers extraction from the sample was limited.

1. Introduction
Extensive researches of organic solar cells have been carried out in various scientific groups. First studies involved relatively expensive and low-efficient methods as evaporation in vacuum [1, 2]. In the last years new concept has been employed – solution processed solar cells [3, 4]. It provides possibility to use low-cost solvent-based printing or spin-coating methods. Successful approach is so called bulk heterojunction solar cell where two materials are mixed together. One of the most popular objects for studies is polymer-fullerene bulk-heterojunction solar cell where poly(3-hexylthiophene) (P3HT) is mixed with [6,6]-phenyl C61-butyric acid methylester (PCBM). This structure typically has efficiency of 3-4% [5]. Investigation of new organic compounds for organic photovoltaic still continues to increase their efficiency and spectral range.

In this paper photoelectrical and photovoltaic properties of three original organic compounds are shown. Ability to form glass-like structure in thin films is main advantage of these compounds. All three compounds have the same electron donor group but different electron acceptor group.

2. Materials
Chemical structure of the investigated compounds is shown in figure 1. All compounds consist of 2-tert-butyl-6-methyl-4H-pyran-4-ylidene fragment as a backbone of the molecule. Each of them contains various electron acceptor groups. Indandione group is in ZWK-1TB molecule, barbituric acid – JWK-1TB and malononitrile – DWK-1TB. Synthesis of the investigated compounds is described elsewhere [6]. Bulky trityloxyethyl group in the investigated compounds supports formation of amorphous state in thin films from organic solvents.
3. Experimental

3.1. Sample preparation
For photoconductivity measurements sandwich type samples with structure ITO/organic layer/Al were made. Organic compounds were dissolved in chloroform with 40 mg/ml concentration. Active layer with the thickness of 500-600 nm was spin-coated on ITO-coated glass at 400 rpm speed for 40 seconds. Then sample was heated at 120°C for 15 minutes. Semitransparent aluminum electrodes with the thickness of 20 nm were deposited by thermal evaporation in vacuum (EDWARD AUTO 306) at pressure of $6 \times 10^{-6}$ mBar.

Samples for photovoltaic experiments were made in sequent steps. PEDOT:PSS layer was spin-coated on ITO-coated glass at 2500 rpm for 80 seconds and dried for 30 minutes at 160°C. Then blended solution was made dissolving our compounds and PCBM in mass ratio 1:1 in chloroform. The solution was spin-coated on PEDOT:PSS layer at 400 rpm for 40 seconds and dried at 120°C for 15 minutes. Finally BaF and aluminum was deposited on top of the active layer by thermal evaporation in vacuum (EDWARD AUTO 306) at pressure of $6 \times 10^{-6}$ mBar. Obtained structure of the samples was ITO/PEDOT:PSS(50nm)/organic compound:PCBM 1:1 (500nm)/BaF(1nm)/Al(70nm).

3.2. Photoelectrical and photovoltaic measurements
Xenon lamp was used as light source in the photoconductivity and photovoltaic measurements. Interference filters in spectral range from 400 nm to 700 nm with step 10 nm and half-width 10 nm were placed in front of the lamp. Average illumination intensity was around 1 mW/cm². The samples were illuminated from ITO and Al electrodes while 1 V positive or negative voltage was applied in photoconductivity experiment. In the figure 2 and 3 it is shown as ITO+, ITO-, Al+ and Al-. Current-voltage characteristics were measured while ITO side was illuminated in photovoltaic experiment. Measurements of the photoconductivity and photovoltaic spectral dependence were performed in vacuum ($1 \times 10^{-5}$ mbar).

3.3. Determination of photoconductivity threshold energy
Charge carriers are strongly localized in organic semiconductor which means that their surrounding becomes polarized. In this way electronic polaron is created [7]. Difference between molecular polaron levels $M^-_p$ and $M^+_p$ is called adiabatic energy gap. These polaron levels $M^+_p$ and $M^-_p$ are actual charge conduction levels in organic material. Adiabatic energy gap value can be estimated from intrinsic photoconductivity quantum efficiency as threshold energy $E_{th}$ [8]. Spectral dependence of photoconductivity quantum efficiency could be used to determinate $E_{th}$ [9].

4. Results an discussion
Photoconductivity quantum efficiency spectrum for JWK-1TB sample is shown in figure 2. Similar
spectra were observed for all the compounds. Minimum of the quantum efficiency at the maximum absorption position indicates charge generation mainly in the volume of the sample [10]. Rising the photoconductivity quantum efficiency values to the power of 2/5 (see figure 3) threshold energy value was obtained. These values are 1.85±0.03 eV and 1.95±0.03 eV for compounds JWK-1TB and DWK-1TB, respectively. It shows that these compounds cover almost all visible light range.

Figure 2. Photoconductivity quantum efficiency and absorption spectra of JWK-1TB sample. Abbreviations explained in section 3.2.  

Figure 3. Determination of the threshold energy of compound JWK-1TB. Abbreviations explained in section 3.2.

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Figure 4. Absorption spectra of the pure film (line) and IPCE spectra of the blend with PCBM (squares) of a) ZWK-1TB, b) JWK-1TB and c) DWK-1TB. d) photocurrent of JWK-1TB:PCBM under 480nm wavelength illumination at various light intensities.

Determination of the threshold energy for the sample with ZWK-1TB was impossible due to very low photocurrent.

Incident Photon to Charge Carrier Efficiency (IPCE) was calculated form obtained current-voltage
characteristics at each wavelength. Obtained IPCE spectral dependences of the organic compound-fullerene samples are shown in figure 4 a, b, c. Correlation between the absorption and IPCE spectra was observed for ZWK-1TB:PCBM which indicates good exciton separation at the interface and charge carrier extraction from the sample. In the case of JWK-1TB and DWK-1TB mixed with PCBM anti-correlation was observed. ICPE has minimum where absorption has maximum. To explain this phenomena photocurrent dependence on incident light intensity at 480 nm (it corresponds to maximum absorption) was measured for JWK-1TB:PCBM (see figure 4 d). Linear dependence was acquired only at low light intensity. Photocurrent rapidly saturates at higher intensity which means that charge carrier extraction is limited. The IPCE efficiency could be greatly increased by overcoming this issue. One of the possible solutions could be thinner active layer.

Maximum short circuit current, open-circuit voltage, IPCE and fill factor is presented in table 1. Almost all parameters are higher for DWK-1TB:PCBM system in comparison with other systems. Only fill factor is lower than for ZWK-1TB:PCBM but it could be increased by optimizing the sample.

### Table 1. Photoconductivity threshold energy $E_{th}$, short circuit current $I_{sc}$, open-circuit voltage $U_{oc}$, Incident Photon to Charge Carrier Efficiency IPCE and fill factor FF of the prepared systems. Number in brackets shows incident light wavelength at which this value was obtained.

| Compound  | $E_{th}$, eV | $I_{sc}$, µA/cm² | $U_{oc}$, V | IPCE max, % | FF max | $I_{sc}$, (490nm) | $U_{oc}$, (510nm) | IPCE max, (530nm) | FF max, (530nm) | $I_{sc}$, (470nm) | $U_{oc}$, (550nm) | IPCE max, (560nm) | FF max, (560nm) | $I_{sc}$, (490nm) | $U_{oc}$, (390nm) | IPCE max, (540nm) | FF max, (540nm) |
|-----------|--------------|----------------|-------------|-------------|---------|------------------|-----------------|------------------|----------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| ZWK-1TB   | ---          | 0.76 (490nm)   | 0.17 (490nm) | 0.3 (510nm) | 0.32 (530nm) |     |
| JWK-1TB   | 1.85         | 1.10 (470nm)   | 0.40 (500nm) | 0.4 (550nm) | 0.21 (560nm) |     |
| DWK-1TB   | 1.95         | 2.50 (490nm)   | 0.60 (480nm) | 1.0 (390nm) | 0.29 (540nm) |     |

5. Conclusions

The threshold energy of photocurrent indicates that glass forming original organic molecules with 2-tert-butyl-6-methyl-4H-pyran-4-ylidene fragment as a backbone can be used to convert visible light to electricity. Photovoltaic effect was observed in all investigated organic compound:PCBM systems. The best results of short circuit current, open-circuit voltage and IPCE were obtained for the compound with malononitrile as electron acceptor group. These results could be improved because generated charge carrier extraction is limited. It could be overcome by preparing thinner active layer.

Acknowledgments

This work has been supported by the ERAF Project No. 2010/0252/2DP/2.1.1.1.0/10/APIA/VIAA/009 and the European Social Fund within the project «Support for Doctoral Studies at University of Latvia»

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