Photovoltaic Effect in Single Layer 1*H*-Pyrazolo[3,4-*b*]quinoline and 1*H*-Pyrazolo[3,4-*b*]quioxaline/Poly(3-Decylthiophene) Polymer Cells

Ewa Gondek[a], Ivan V. Kityk[b], and Andrzej Danel[c]

[a] Institute of Physics, Technical University of Cracow, Podchorazych 1, Krakow, Poland
[b] Electrical Engineering Department, Technological University of Czestochowa,
Al. Armii Krajowej 17/19, Czestochowa, Poland
[c] Department of Chemistry, Agricultural University of Krakow, ul. Balicka 122, 31-149 Krakow,
Poland

Reprint requests to E. G.; E-mail: e.gondek@wp.pl

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We have explored photovoltaic (PV) reponse for the pyrazoloquinoline and pyrazoloquinoxaline dyes incorporated into the poly(3-decylthiophene) (PDT) polymer matrices. The photovoltaic response correlates generally with the enhancement of the state dipole moments. Generally we have shown that enhanced state dipole moments lead to an increase of the open circuit voltage. The surrounded polymer matrix of the polythiophene enhances the ground state dipole moments and its relative changes are decreased with the increase of the particular state dipole moments. An appearance of the three-phenyl backside groups substantially diminishes the effect.

Key words: Photovoltaic Effect; Pyrazoloquinoline.

1. Introduction

At present organic materials are used in numerous electronic devices. The most important include organic light emitting diodes (OLED) based on simple molecules [1 – 3], oligomers and dendrimers [4, 5] or polymers [6, 7]. The other ones are organic field effect transistors (OFET) [8, 9]. Inorganic compounds are much more durable and stable towards moisture, oxidation or temperature. On the other hand, organic synthesis offers tools for modification of materials' properties and creating a huge area for lower manufacturing costs.

The investigation of organic photovoltaic devices is more promising with respect to inorganic PV. Organic semiconductors are less expensive than their inorganic equivalents and easy to manufacture. Thin film cells possessing a single donor/acceptor interface have shown a possibility to achieve photovoltaic efficiency equal to about 5% [10].

One of the principal advantages of these devices is their cheaper manufacturing with respect to the semiconductors, however, the drawback of such devices is low lifetime together with the still insufficient performance. Despite extensive work on the topic [11 – 16], there is no general conception how to change their physical-chemical parameters to achieve enhanced photovoltaic (PV) response.

It is known that one of the main parameter is the open circuit voltage (V_{OC}), which is proportional to the difference between the highest occupied molecular orbital of the electron donor ($HOMO_D$) and the lowest unoccupied molecular orbital of the electron acceptor ($LUMO_A$), i. e. $\Delta(HOMO_D\text{-}LUMO_A)$. Moreover for the case of the heterojunctions some Fermi level pinning between organic materials and surface charges has been proposed [17, 18]. Additionally, operating by thin layers on the interface between the organic semiconductor and the aluminum electrode one can enhance charge separation [18]. In this case a promising way is an application of the thin aluminium oxide layer at the interface organic material/aluminium [19]. However, it is clear that there are other factors that are more difficult to be taken into account, like hole mobility, exciton diffusion lengths etc. One can expect that they will be more sensitive to the polarizability of the particular dye chromophore and their effective interactions with the hole-transporting polymer matrix. The problem of such investigations is that we have a superposition of different factors. As a consequence the contribution of each such factor is difficult to evaluate.

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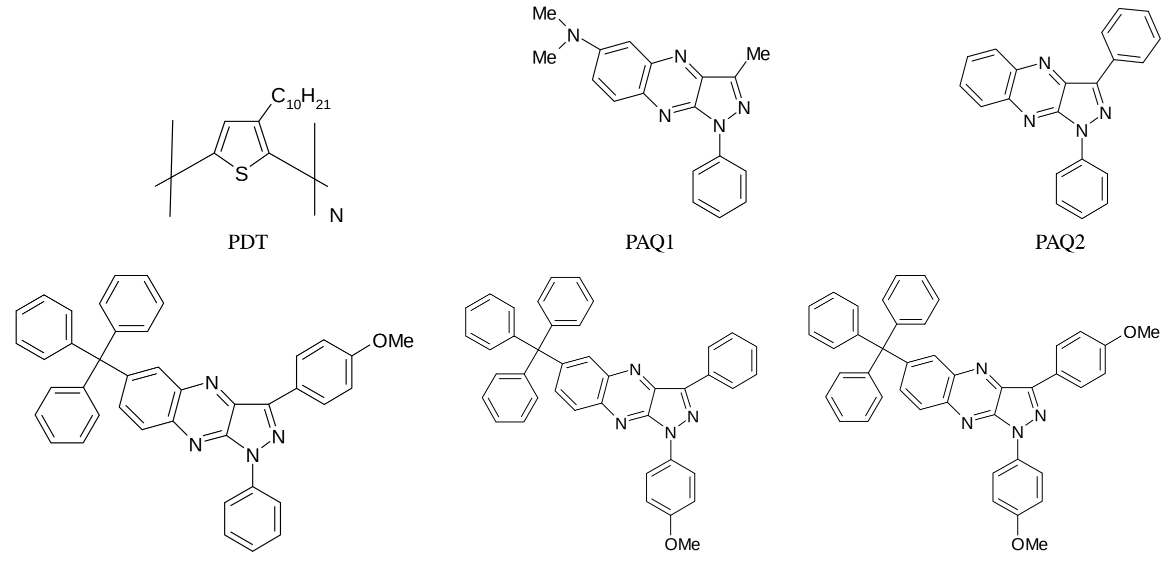


PDT PAQ1 PAQ2

PAQ3 PAQ4 PAQ5

Fig. 1. Chemical structure of
PDT: Poly(3-decylthiophene-4,5-diyl),
PAQ1: 3-Methyl-1phenyl-6-*N*,*N*-dimhetyleamine-1*H*-pyrazolo[3,4-b]quinoxaline,
PAQ2: 1,3-Diphenyle-1*H*-pyrazolo[3,4-b]quinoxaline,
PAQ3: 3-(*p*-Methoxyphenyl)-1-phenyl-6-trityl-1*H*-pyrazolo[3,4-*b*]quinoline,
PAQ4: 1-(*p*-Methoxyphenyl)-3-phenyl-6-trityl-1*H*-pyrazolo[3,4-*b*]quinoline,
PAQ5: 1,3-(*p*-Methoxyphenyl)-3-phenyl-6-trityl-1*H*-pyrazolo[3,4-*b*]quinoline.

Oligo- and polythiophenes are organic materials with a wide range of application including sensor films, antistatic and recording materials, rechargeable compounds, electrochromics OFET and OLED materials. For the first generation of polythiophene numerous synthetic methods were developed to prepare polythiophenes with established optical and physical properties. Oxidative coupling of 3-alkylthiphenes with iron(III) chloride is a very simple synthetic method but produces regiorandom polymers. On the other hand McCullough and Rieke developed a method to synthesize regioregular poly(3-alkylthiphenes) [20–23]. The aspect of regioregularity in polythiophenes plays an important role in their band control. In our investigation we applied poly(3-decylthiophene) (PDT) with regioregular structures as donors. These allow to obtain a partial orientation of the films.

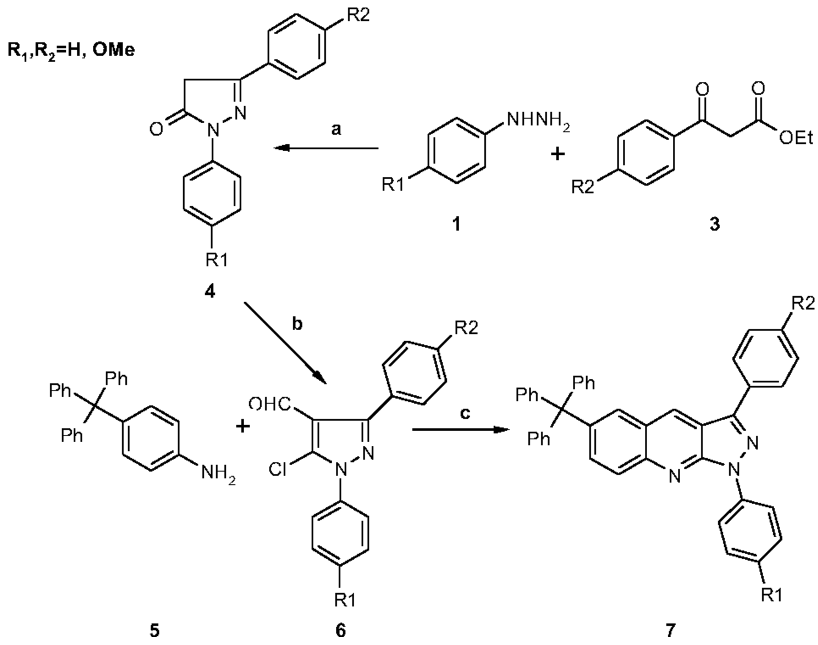
As dye chromophore acceptors we use in this work pyrazoloquinoline and pyrazoloquinoxaline derivatives which have demonstrated excellent optoelectronic properties [24]. A promising opportunity for this dye chromophore is a possibility to operate on their ground state dipole moments at slightly varied values of HOMO and LUMO energy positions. This may give a good opportunity to operate on principal technological parameters like V_{OC} by changing the ground state dipole moments.

2. Experimental Section

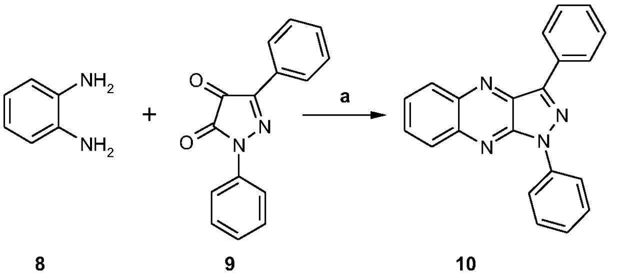
2.1. Materials

Regioregular poly(3-decylotiophene-4,5-diyl) was purchased from Aldrich Chemicals. The employed organic compounds and their indications are shown in Figure 1.

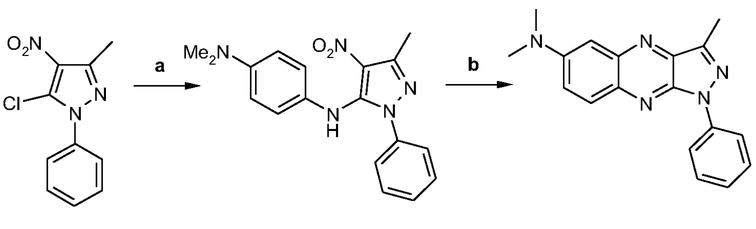
Since the synthesis by Musierowicz, Niementowski, and Tomasik the first example of 1*H*-pyrazolo[3,4-*b*]-quinoline (PAQ) of that class of compounds was investigated mainly from the medical point of view [25]. In the sixties of the 20th century some papers on optical brighteners based on PAQs have been published [26]. The majority of pyrazoloquinolines exhibit strong photoluminescence in solution and in the solid state as well. So we decided to use them in organic electroluminescent devices [27]. The organic materials used in these devices should be a stable compound with high melting points T_m and glas transition temperatures



Scheme 1. a) EtOH/boiling/1 h; b) DMF/$POCl_3$/110 °C/1 – 2 h; c) melting/140 – 210 °C.



Scheme 2. a) boiling, glacial acetic acid/12 h.



Scheme 3. a) K_2CO_3/p-N,N-Me-aniline/DMF/120 °C; b) $FeC_2O_4 \times 2H_2O$/sulpholane/5 min/250 °C or $P(OEt)_3$/12 h.

T_g and should form stable amorphous pine-hole free films after vacuum evaporation or spin-casting. The stability of organic layer is very crucial for optoelectronic devices. Several classes of glass-forming small molecules with high T_g and T_m have been synthesized. The most important ones are star-burst molecules, dendrimers, spiro and cardo molecules, and tetrahedral systems.

We introduced trityl groups into a PAQ skeleton to increase thermal resistance of luminophors and used them in OLED's and PV devices.

The general synthesis is outlined on the Scheme 1. *p*-Trityl aniline **5** was reacted with 5-chloro-4-formylopyrazoles **6**. The last one was easily prepared by chloroformylation of pyrazolones **4**.

1*H*-pyrazolo[3,4-*b*]quinoxalines **10** and **13** have been prepared in a different way. The first way of the synthesis is the condensation of o-phenylenediamine **8** with 2,5-diphenyl-2H-pyrazole-3,4-dione **10** in boiling glacial acetic acid (Scheme 2) [28]. The second route is a reductive cyclisation of nitropyrazole **12** with iron oxalate or triethyl phosphite (see Scheme 3) [29].

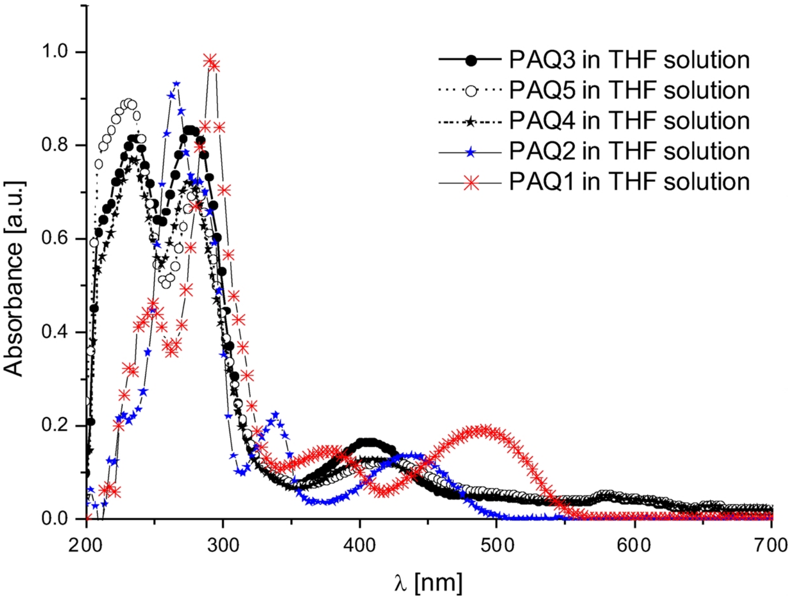


Fig. 2. Absorption spectra of PAQ chromophore in THF solution [30].

3. Calculation Procedure

As a basic quantum chemical method we used Becke's three-parameter exchange functional with gradient-corrected functional of Lee, Yang, and Parr (B3LYP) density functional method on a 6-311+G (3df) level which has shown its efficiency during investigations of the pyrazoloquinoline derivatives incorporated into the polymer matrices [24]. At the beginning we did MM+ force field method optimization of the studied chromophore. Firstly the simulations were done for the isolated molecule. The increment of time convergence was equal to about 1 ps. The optimization was performed by the layer-by layer covering of the initial molecule by surrounding PDT polymer chains and was continued up to the achievement of the total energy convergence within the value of about 0.0025 eV. It is principal that the number of polymer layers do not influence substantially on the convergence of the eigenenergies. The electronic charge density was calculated assuming the effective center of electronic charge mass to be situated at the center of the dye chromophore. Varying the distance between the chromophore and the surrounding polymers we found a minimum of total energy. Such optimized conformation has been assumed to be more stable and therefore was chosen to be the basis of all the calculations.

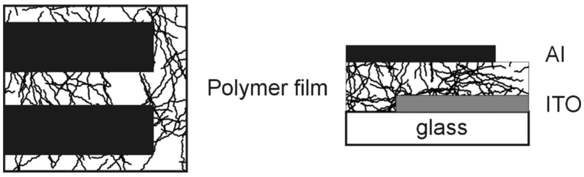


Fig. 3. Principal sketch of the photovoltaic cell sandwich.

3.1. Cell Fabrication and Photocurrent Measurements

The PDT was used to provide the photoexcited electron donors. The PAQ served as acceptor. Devices were fabricated on glass/ITO slides, which were thoroughly cleaned in an ultrasonic bath using organic solvents. The organic photovoltaic cells were fabricated in the basic architecture: ITO/Active Layer/Al. The active layer (blend of PDT and PQ 1 : 1) was deposited by spin-coating in a tetrahydrofurane solution. The average thickness of the active layer was estimated to be about 150 nm. Current-voltage (I-V) characteristics of the device were measured using a source-meter (Keithley 236). It is known that enhancement of the absorption in the visible spectra range should enhance the PV efficiencies. Following Figure 2 one can see that the device was illuminated at a maximum light intensity of 1.3 mW/cm^2. The overall architecture of the device is presented in Figure 3.

Table 1. Photovoltaic parameters for ITO/PAQ+PDT/Al solar cells.

Layer sequence	V_{OC} [V]	J_{SC} [A/cm^2]	FF	R_S[MΩ]	R_{SH}[MΩ]	QE (%)	M(D)	MM(D)
PAQ2+PDT	0.705	30,097	0.22	1.69	1.76	0.35	2.102	2.189
PAQ1+PDT	1.084	27.543	0.185	1.49	2.14	0.42	4.632	4.689
PAQ3+PDT	0.132	0.269	0.251	1.21	1.90	0.07	0.378	0.589
PAQ5+PDT	0.992	2.139	0.155	0.72	2.04	0.02	1.386	1.423
PAQ4+PDT	0.510	2.77	0.252	1.46	1.14	0.02	0.832	1.121

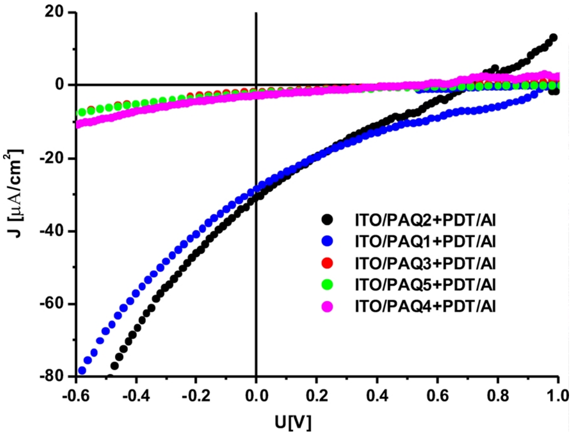


Fig. 4. I-V characteristics under illumination of ITO/active layer/Al devices P_{light} = 1.3 mW/cm^2.

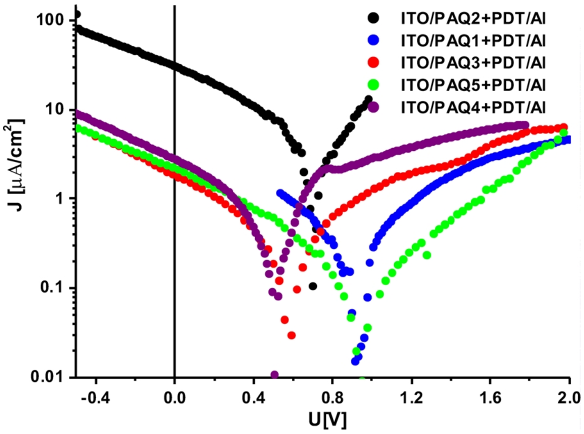


Fig. 6. Current-voltage (J-V) characteristics of devices with ITO/active layer/Al represented in the semi-log scale.

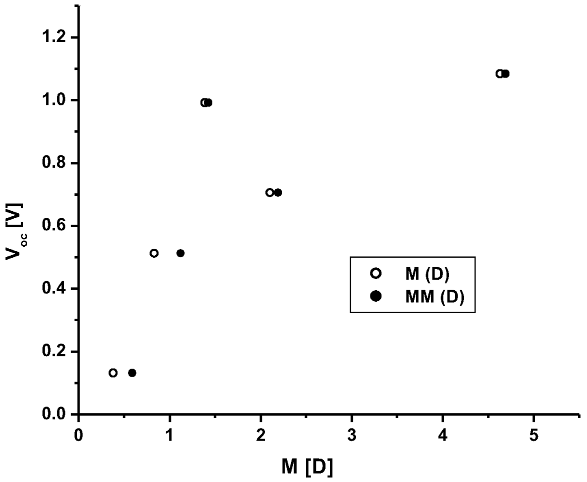


Fig. 5. Dependence of V_{OC} versus ground state dipole moments of dye chromophore molecules. M(D) – corresponds to the ground state dipole moment of the isolated molecule; MM(D) – the same for the chromophore incorporated into the polymer matrix.

4. Results and Discussion

In Figure 4 current-voltage characteristics of the investigated materials under the illumination of light with power density 1.3 mW/cm^2 are presented. One can see a principal difference between the PAQ1 and PAQ2 containing composites which may reflect the influence of the backside triphenyl group. To study the influence of ground state dipole moments we represent in Figure 5 the dependences of V_{OC} versus ground state dipole moments of isolated dyes and chromophore incorporated polymer matrices. One can see an increase of V_{OC} with the increasing values of dipole moments. For reader's convenience we have listed the principal parameters in Table 1, some of them are defined in Figure 6. Following the performed molecular dynamics/quantum chemical calculations we have included the values of ground state dipole moments for the isolated molecule and for the molecule covered by polymers as well.

Table 1 presents the PV parameters for single-layered photovoltaic cells consisting of ITO/PAQ+PDT/Al, where PAQ and PDT are the active organic materials. Photovoltaic parameters: short circuit current density J_{SC}, open circuit voltage V_{OC}, fill factor FF, shunt resistance R_{SH}, and serial resistance R_S.

Assuming that the HOMO levels of the PDT is about −5.26 eV and the LUMO levels about −2.87 eV, so one can see that the difference between the HOMO and LUMO levels of the donor chromophore are sub-

Table 2. HOMO and LUMO calculations for the PDT matrices.

PAQ in PDT matrix	PAQ1+PDT	PAQ2+PDT	PAQ3+PDT	PAQ4+PDT	PAQ5+PDT
$HOMO_0$ [eV]	−5.32	−5.48	−5.33	−5.37	−5.46
$LUMO_0$ [eV]	−2.68	−2.63	−2.64	−2.69	−2.45

stantially lower than the corresponding difference of the ground state dipole moments. But the photocurrent densities of these cells are quite low. It is well known that the value of the open circuit voltage is affected by the photocurrent density (see [31]). Moreover, one can see that the enhanced ground state dipole moments causes enhanced V_{OC} and J_{SC}. One can expect that the polarized PQ chromophores cause additional orientation of the polymer chains. As a consequence we have more effective space charge separation due to occurrence of the long-range ordering. An exception presents the sample PAQ5, which also show substantial changes of the HOMO and LUMO positions. This fact confirms the assumption that, when we have the close energies of the HOMO and LUMO levels, the ground state dipole moments play a dominant role. However, when the HOMO and LUMO levels are close and when their values are low, one can say that in this case the difference $\Delta(HOMO_D\text{-}LUMO_A)$ begins to play a more substantial role, which is substantially less for the PAQ5 compared to the other compounds. So the two parameters – Δ and values of the ground state dipole moments – should play a crucial role in the PV response of the devices. It should be added that transition and excited dipole moments do not show any correlation with the observed V_{OC} and J_{SC} features. Another factor is the fact that the ground state dipole moments do not only influence the V_{OC}, however, probably influence the short current J_{SC} features. From Table 1 one can see that these factors are crucial due to the different carrier transport kinetics. The maximally achieved value of PV efficiency of 0.42% shows the possibility to continue the molecular engineering research by varying the backside groups of the chromophore and by improving the hole transport properties of the polymers to achieve an enhanced quantum efficiency. It is principal that the incorporation of the chromophore into the polymer matrices leads to an enhancement of the energy position for the HOMO and LUMO levels. With the increasing absolute value of the ground state dipole moments the difference between the ground state dipole moments of the isolated molecule (M) and those of the molecule incorporated into the matrices (MM) decreases. This may reflect an enhancement of the local electrostatic fields restraining the contribution of the external polymer chains. Comparing the results presented in Table 1 and 2 one can conclude that the difference for the HOMO and LUMO energy levels for different dye chromophores is less than a variation of the ground state dipole moments. This is very crucial because in this case one can expect that these values (ground state dipole moments) would play a principal role.

It is well known that one of the principal parameters for such devices is their stability with respect to oxidation, humidity etc. These factors determine their degradation and aging stability [32]. One of the advantages of the investigated chromophores is that they are stable with respect to oxygen. So one can expect that this factor may be one of their benefits compared to other dye chromophores.

The achieved efficiency (0.42%) is not too relevant for practical applications, however, this coefficient is substantially larger than the efficiency of 0.28% achieved for the PAQ in the PDT matrices [32]. So the main strategy of the search and design of enhanced PV response should be directed on a synthesis of materials with the enhanced ground state dipole moments and varying the polymer matrices. One can guess that in the last case principal role will play the transport hole kinetics of the polymer matrices and the charge separation aspects.

Finally it is to emphasize that in [33] it was predicted that the ground state dipole moments may have substantial influence on charge separation. However, they have not find a direct correlation with the PV efficiencies. That means that for different compounds the role of the state dipole moments may be disturbed by another factor. A principal role may here belong to relative dipole-dipole interactions between chromophore-chromophore and chromophore-polymer chain.

5. Conclusions

We have established the principal influence of the triphenyl backside groups on the output of photovoltaic efficiency. The photovoltaic response correlates with the enhancement of the ground state dipole moment's values. We have established that enhanced ground state dipole moments lead to the increase of the open circuit voltages. The surrounding polymer matrix of the polythiophene favours an enhancement of the ground state dipole moments. The appearance of the triphenyl backside groups diminishes the PV efficiency. An exception presents the sample PAQ5, which simultaneously shows substantial changes of the HOMO and LUMO energy positions and this fact confirms that, when we have the close energy parameters of the HOMO and LUMO, one can say something about the dominant role for the ground state dipole moments. However, when the HOMO and LUMO levels are close the difference $\Delta(\mathrm{HOMO_D}\text{-}\mathrm{LUMO_A})$ begins to play a modified role, which is substantially less for the PAQ5 compared to the other chromophores.

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