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PHYSICAL ORIGIN OF PHOTOVOLTAIC EFFECTS IN CYANO SUBSTITUTED PYRAZOLOQUINOLINES

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SINGLE LAYERED PHOTOVOLTAICS BASED ON CYANO SUBSTITUTED PYRAZOLOQUINOLINE CHROMOPHORES

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Abstract: An increase of efficiency of the single layered photovoltaic based on cyano substituted pyrazoloquinolines chromophore up to 0.44 % was achieved. We analyze role of incorporated chromophore in changes of effective exciton radius lengths formed by Coulombic chromophore_polymer interactions using the density functional theory (DFT) theoretical quantum chemical simulations. We show that both ground state dipole moments of chromophore as well as their electrostatic interactions with the conjugated conducted polymer chains play here an important role. In particularly, we have found that incorporation of the highly polarized cyano group leads to enhancement of the state dipole moments and open circuit voltage up to 1.107 V. That means the enhancement at least by 40 % compared to the pyrazoloquinoline without the cyano groups. At the same time the excitonic length determined by chromophore-matrix and polaronic effect demonstrates more strong correlation with the observed PV efficiencies.

1.INTRODUCTION

Recently, one can observe an enhanced interest to organic photovoltaic cells [1-3]. It is well known that the principal parameter of the photovoltaic (PV) response - open circuit voltage V_{oc} value increases, as expected, in-line with the difference between the higher occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor. There exist different reserve to enhancement, in particularly due to

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3 formation of a thin Al_2O_3 layer at the organic acceptor/aluminium interface, favouring the
4 shunt resistance of the device and preventing chemical reaction between aluminium and the
5 organic material [4] and use of different oxides, first of all titanium with porous structure.
6 Main efforts are directed on an optimization of the photo-carrier transport and photovoltaic
7 effects of the Schottky junction cell consisting of indium tin oxide/organic/polymer films/Al.
8 The first stage requires an existence of effective chromophore possessing large absorption
9 within the spectral range of the visible (VIS) light. The second stage is a formation of hole-
10 electron Coulombically bounded excitons propagating from the transparent indium-tin oxide
11 (ITO) electrodes towards metallic cathodes. The length of the exciton existence (so-called
12 excitonic lengths) will be determined both by the binding energy of the polymer matrix
13 exciton, chromophore and first of all by their dipole-dipole interactions. Particular role here
14 play polymer chain length, regioregularity and film thickness [5].
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26 The photocurrents of the cell based on the excitation spectra with respect to their
27 illumination sides are closely related to the carrier generation mechanisms. Additionally
28 crucial role here begin to play modifications of the energy HOMO-LUMO positions of
29 principal acceptor-donor groups and number of polymer side chains [6] defining exciton
30 mobility. The first single layered-organic PV devices possessed a thin organic film situated
31 between cathode and anode [7]. Their PV efficiency is determined by work energy of
32 electrode and hole mobility of the basic organic polymer usually of p-type. Formation of
33 double-layered architecture proposed in the Ref. 8 was a next step to improve of the all-
34 organics PV cells. Developing this technology PV efficiency was improved up to power
35 conversion efficiency about 1% [9]. Additionally this double-layer technique used to a
36 conjugated polymer evaporating C_{60} acceptors on top electrode. For such architecture
37 excitons were formed in the conducting polymer layer after photo-absorption in the VIS
38 spectral range. The principal mechanism of exciton migration is realized through the hopping
39 between conjugated chain fragments of the conducting polymer chains. Annihilation of
40 excitons has taken a place nearby polymer/ C_{60} heterojunction, after that the electron is
41 transmitted to the high electron affinity C_{60} layer. So to separate electron and holes from
42 excitons materials with strong acceptor properties like fullerenes was applied. Afterwards
43 carrier transport of the excitonic dissociated holes and electrons (holes in the polymer and
44 electrons in the fullerene) is performed. And finally there appears the free charge carrier
45 collection at the appropriate electrodes. It is clear that in this case principal role begin to play
46 effective excitonic diffusion lengths and carrier mobility.
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Principally new possibilities for operation by the main kinetics parameters of the PV may open an operation by the transport properties both of excitons as well of the dissociated electrons and holes, which are relatively small in sizes chromophore possessing large absorption in VIS and simultaneously having moderate state dipole moments. Due to the chromophore-polymer chain interactions they can change the process of the photogenerated transport in the desired direction depending on the values of the state dipole moments and principal HOMO/LUMO levels.

Among a dozens of organic chromophores, pyrazoloquinoline molecule may present an especial interest due to their relatively low sizes, good complimentary with respect to the polymer matrices, opportunity to change the ground state dipole moments by appropriate substitution of the backside chemical groups. Despite they have large absorption within the wide visible spectral range [10,11]. Their properties are determined by effective dipole-dipole interactions of them with the polymer matrix chains due to electrostatic Coulombic interactions. The latter one define effective exciton diffusion length [12]. For PV devices it is essential to convert excitons into charge carriers. However, principal role here also belong to the disordering of the basic conducting polymer, which determines its binding energy and the carrier kinetics. So the transport (by diffusion) of excitons to the heterojunction plays a principal role in the operation of an organic solar cell. A widely used method to study exciton diffusion is based on interface quenching in which the reduction of fluorescence lifetime is studied by a quenching layer [13]. However, more effective to perform the molecular dynamics and quantum chemical simulations of the particular chromophore during their illumination by external light. In our earlier works we have shown an efficiency of molecular dynamics and quantum chemical methods to predict principal parameters of the pyrazoloquinoline derivatives [14]. Introduction of the low-sized chromophore like pyrazoloquinoline may be very effective method to operate by the exciton diffusion length. This is caused by their low sizes allowing to incorporate them very closely to the most of polymer chaines which give efficient chromophore-polymer interactions. In this case one can not to exclude difficulties of investigations of the luminescent kinetics with picosecond resolution. Moreover due to the relatively large electron-vibration interactions (closely related to polarons) these chromophore may be an additional reserve to operate by exciton kinetics by appropriate changes of their concentration and polarizabilites due to incorporation of chromophore with different polarizabilities. It is crucial that in this case we can work in single layer PV achitecture [15].

Recently we also have shown [16] that incorporation of the pyrazoloquinoline (PQ) derivative materials into the hole conductive polymer matrices gives a possibility of their application as PV chromophores in the single layered architectures. Moreover, a general tendency was established, that with enhancement of the ground state dipole moments for particular chromophore one can achieve an enhancement of the open circuit voltage – V_{oc} . Following this finding in the present work we have synthesized molecule with state dipole moments varied in the wide range due to addition of cyano atoms. We perform study of traditional current-voltage features during illumination by visible light with moderate power densities. The performed quantum chemical calculations have shown, that even without taking into account of the surrounding matrices changing the particular ground state dipole moments [17], a sufficiently good correlation between the open circuit voltage and values of the state dipole moments is observed. We have achieved almost the two times enhancement of the open circuit voltage playing a main role in the PV response efficiencies.

In the Ref. 18 it was shown that principal role in the behavior of the open circuit voltage for the case of the bilayer architecture play difference between the energies of HOMO of donor and the LUMO of acceptor. In the case of the single layered pyrazoloquinoline chromophore the principal role also may play energy positions of the HOMO energy levels. So, in this work we will try to modify the values of ground state dipole moments to achieve the enhanced ground state dipole moments by incorporation of cyan complexes. At the same time we will explore a possible influence of the HOMO energy positions of chromophores on the observed dependences.

The short-circuit photocurrent of organic and some inorganic solar cells increases with increasing light intensity, P_{in} , and can be expressed as $J_{sc} \sim I^{\alpha}$, [19] where α is a function of the ratio of the thermally created to photogenerated carrier concentrations. At low intensities $\alpha=1$, and at higher intensities $\alpha=0.5$ [19].

In the present work we perform studies of single layer PV cells in the geometry ITO/Polymer+PAQ/Al. The experimental part is presented in the Section 2; Section 3 describes the dependence of the effective PV response versus the chromophore ground state dipole moments and effective diffusion lengths of excitons calculated without and with taking into account of the polaronic effects determining by electron-vibration trapping levels.

2. EXPERIMENTAL PART

Synthesis of chromophores

Pyrazolo[3,4-*b*]quinolines substituted with bromine **1** were synthesized by condensation of *p*-bromoaniline with 5-chloro-4-formylpyrazoles following the method given in ref.. 20. Bromo

derivatives were transformed into nitriles **2** by Rosenmund-von Braun reaction (heating of aryl bromides with an excess of CuCN in high boiling polar solvent). The detailed technological procedure and analytical data are given elsewhere [21,22]. The same procedures were used for synthesis of compounds substituted with *N,N*-Me group. [23,24]. Generally scheme of synthesis is depicted on the Scheme 1.

Scheme 1. a) CuCN, NMP, 190 °C.

Poly(3-decylthiophene-2,5-diyl) PDT conducted polymer with regioregular structures was purchased from Aldrich.

Photovoltaic device preparation.

PV devices were manufactured on glass /ITO slides, which were thoroughly cleaned in an ultrasonic bath using toluene. Their surfaces were 15 x15 mm.

The films were deposited by spin coating from tetrahydrofuran solutions of mixture of PDT and pyrazoloquinoline (PAQ) (1:1). The average thickness of the active layer was estimated to be about 150 nm and following AFM control the surface roughness did not exceed 2-4 nm; The photovoltaic cell configuration was ITO/PDT+PAQ/Al (fig.5.). Aluminum electrode was evaporated on the surface of polymer under high vacuum conditions and had a thickness about 60 nm.. The photocurrent as well as current-voltage (IV) dependences were measured using the Keithley 2400 source meter.

The parameters to perform the PV response efficiency evaluations are given in Fig. 3. They are defined below:

- The open circuit voltage V_{oc} - is the voltage on the I-V curve at zero current.
- The short circuit current, I_{sc} , is the current on the I-V curve at zero voltage.
- The fill factor (FF) is determined by an equation :

$$FF = \frac{\text{Voltage at peak power } (V_{pp}) * \text{Current at peak power } (I_{pp})}{\text{Open circuit voltage } (V_{oc}) * \text{Short circuit current } (I_{sc})}$$

- The energy conversion efficiency (η) is given by :

$$\eta(\%) = \frac{V_{oc} * I_{sc} * FF}{\text{Total power of light radiating on the cell area}} * 100$$

3. RESULTS and DISCUSSION

Traditional current-voltage dependences for the investigated chromophore at moderate light are depicted in the Fig. 2 and Table 1. It is crucial that with enhanced value of ground state dipole moments we usually have an enhanced open circuit voltage V_{oc} . Some deviations from this rule occurs for the sample 4 (Mol3+PDT) and it may reflect a larger energy shift in the positions of the HOMO levels. Simultaneously it is not observed an obvious correlation between the short current I_{sc} and the state dipole moments or calculated energies of the HOMO-LUMO levels of chromophore. Comparing to the former chromophore without the cyano groups addition one can see that the values of the open circuit voltages are at least two times larger. At the same time the short currents do not show such correlations. Principal mechanism here is photoinduced charge transfer. One can expect that the principal mechanism consists in formation of excitons prevailing by the PQ donors. The transport of excitons is determined by their effective radius, which is strongly dependent on the dipole-dipole interactions PQ chromophore-polymer chain defining the binding energies. For this reason we have done calculations of the effective exciton radius closely related to the exciton diffusion lengths for the investigated chromophore using a method described in the Ref. 11. We have assumed that the chromophore are incorporated into the effective polymer matrix space, which is assumed to be regioregular. Additionally we have calculated re-normalization of the effective exciton radius due to occurrence of effective polaronic states caused by electron-vibration interactions as described in the ref. 11. On the other hand, the PL spectra of

many transport p-conductive polymers show distinct emission bands that are generally attributed to electronic transitions accompanied by vibronic (quasi-phonon) repercussions at lower energies. The performed by us PL measurements have shown that there are not strictly mirror symmetry for absorption - luminescence , which indicates on existence of trapping relaxation effective cross-section processes in the excited states. This fact can be an indicator of disorder presenting in the polymers, leading to a localization of the electronic wave function and a strong inhomogeneous broadening of the optical transition. At the same time this fact reflects several influence on the excitons of the effective chromophore-polymer interactions changing the kinetics of the excitons and other free carriers. After excitation into higher lying states of the non-homogeneously widened transition. The relaxation processes preferentially populate the states with lower energies. The radiation transition to the ground-state occurs from the lower lying level of the density of states (DOS).Additional mechanism of exciton destroying may be their thermalization how it is described by a model [26],assuming exciton thermalization like hopping in a DOS to be approximated by a Gaussian distribution of energies . All these approaches do not consider role of chromophore substantially renormalizing the process due to chromophore-polymer interactions.

So we have the traps of different origins. The exact nature of the traps is not clear up to the end. Several models consider presence of electron capturing carbonyl groups. Nearby these levels there are vibronic replica, additionally there are excitonic levels originating from Coulombic chromophore-polymer interactions.

It is crucial that for molecular like crystal to which one can to account the investigated composites prevailing are exponentially distance dependent hopping rates, favouring phonon-assisted (polaronic) tunnelling process rather than dipole-dipole energy transfer.

Since the discovery of the light stimulated electron transfer from a conducted polymer to acceptor molecules, closely related to the introduction of the bulk heterojunction approach, this material combination has been extensively studied in organic solar cells achieving PV efficiencies up to 5 %. However, there exist substantial limiting factors caused by charge-carrier transport due to carrier scattering thermalization etc. and photogeneration features. Organic PV materials on the base of PDT have relatively low dielectric constant and a high

exciton binding energy, unlike inorganic semiconducting materials. Consequently, the ambient thermal energy is not sufficiently enough to dissociate a photogenerated exciton with binding energies within 0.4- 0.5 eV into free charge carriers.

Another crucial mechanism is a morphology of the thin layers where we have the excitonic annihilation. The transport of electrons/holes in such films is a crucial parameter and is very sensitive to the morphology which should have a roughness below 5-7 nm at least. Main strategy should be directed on production of thicker films to enhance the absorption, without increase of recombination losses. An optimized transport of electrons and holes in the efficient films is required to suppress the build-up of the space-charge that will significantly reduce the power conversion efficiency [27]. Dissociation of electron-hole pairs at the donor/acceptor interface is a principal limiting factor under normal operation condition and its time resolution seems not to be too quick.

Rothberg and co-workers, have established that photoexcitation prevailing leads to the generation of inter-chain polaron pairs [28, 29]. Polaron pairs (electron autolocalised by vibration deformed cloud) are significantly different from excitons in the sense that the excited electron and hole are space separated onto adjacent chains (conjugated fragments). With their characteristic chain deformations the pair consists of essentially a negative polaron P^- and a positive polaron P^+ bound by Coulomb attraction. Sometimes such kinds of quasi-particles are also titled indirect excitons or charge transfer excitons.

Taking into account the role of chromophore state dipole moments determining polarizability induction on the polymer chains it should be emphasized that they play crucial role in polymer self-ordering [30], charge transport, mean transit time [31] etc. However frequently it is considered as a function of HOMO (LUMO) energy positions [32] without consideration of charge transfer and Columbic interactions between the transport polymer and chromophore. The latter should be sensitive to the dipole moments. So searching the enhanced values of the HOMO - LUMO differences [33] it is almost completely ignored the polymer chain – chromophore charge transfer and the corresponding exciton kinetics.

Exciton photogeneration is accompanied by exciton space migration and charge separation at the donor/acceptor interface for the bilayer architecture. However, for the single layer devices such border is absent and the process is expected to be randomly distributed through the effective PDT/PQ film.

It is well known that the exciton diffusion length in a conjugated polymer is usually less than the photon absorption length (more than 400 nm), the quantum efficiency of a bilayer PV device is restrained by the number of photons to be able absorbed in the effective exciton diffusion range and at the polymer/electron acceptor border.

Thus, the efforts should be directed on modification of chromophore polarizabilities strictly connected to the ground state dipole moments, their sizes and morphology [34] with the follow formation of multi-layered structure [35], where principal role belong to difference HOMO-LUMO energies for donor-acceptor, respectively.

Generally the excitonic transport plays a crucial role in the operation of polymer-based optoelectronic devices. Although the efficiency of device PV has been considerably improved, the understanding of the physical principles device operation is not yet complete and is very often controversial. For example, origin of photoinduced carrier hopping between trapping states formed on the borders polymer-chromophore in disordered and partially-ordered conducted polymers, direction of preferential directions for exciton diffusion, what kind of chromophore (sizes, values of ground dipole moments polarizabilities) should be incorporated to modify the carrier mobility on the polymer chains, what concentration of the chromophore is optimal; chemical modifications of the backside groups etc. For the single layer architecture principal question is about a role played by exciton diffusion in the quenching of excitons near the cathode.

In our case we deal with hole transport materials (PDT and PQDs). The incorporated chromophore can only operate by the exciton transport kinetics and the collection of transport carriers near the cathodes. As a consequence there is not a donor-acceptor interface for charge separation as for multi-layered devices. and it may be difficult to perform separation of hole-electron pairs for charge carrier generation. In traditional polymer blends, this photoinduced electron transfer is durated up to 15-20 fs, and the back transfer is durated several ms [36.]. The exciton diffusion length determines the size of the polymer phase which is effective in the charge carrier generation process. Enhanced exciton diffusion is allowed for larger polymer thickness, hence for an increase of the fraction of polymer in the blend, which in turn gives rise to an increased absorption (in the case of a weakly

Moreover, if even the electron-hole pairs may be separated, it is not yet ensured that transport electrons to the electrode will be accelerated. For the such kinds of materials the only explanation may be given within the polaron mechanisms described within the electron-phonon coupling effectively introduced by Frohlich [37]. Following this approach the polaron states favor occurrence of the collective excitation similarly to the polaronic conducting mechanisms [38].

The exciton diffusion lengths in various conjugated polymers reported in the literature show a large variation, ranging from 5 to 14 nm. Most of these studies make use of a bilayer model system, comprising an evaporated C60 layer in combination with a conjugated polymer, spin-coated from solution.

Its efficiency should be very crucially dependent on the polarizability of the matter strictly related to the state dipole moments of the composites. So with enhancing of the particular dipole moments of the compounds and their polarizability one can operate by the such charge separation which is closely related to the open circuit voltage V_{oc} .

In this case we try to achieve additional possibility to enhance the open voltage circuit. A complication when applying the diffusion model is that the luminescence decay in conjugated polymers cannot be characterized by a single exponential with lifetime τ .

TCSPC measurements show a non-monoexponential decay of the neat polymer film luminescence. There may be several reasons forming such non-exponential decay. After illumination of PV devices through transparent ITO electrodes the first transport mechanism should be prevalingly intra-chain [39]. During propagation through the corresponding chains the exciton begin to interact with different trapping levels formed by inter-chain exciton states. As a consequence the living times of the excitons is drastically increased. At longer lifetimes a different type of metastable exciton, e.g. inter-chain excitons, will give more contribution play an increasing role in exciton dynamics. When the polymer is doped by chromophore with moderate dipole moments in this case we will have two substantial modification of the kinetics. The first one will be related to formation of the inter-chain excitonic states and the second one will be associated with the change of the effective number of free carriers. However, more important is a fact that for the single layered devices inter-chain Coulombically bound electron-hole (polaron) pairs are formed [40,41.], describing the photophysics of an excimolecular state. Exciton renormalization by back transfer from polaron pairs is manifested with different rates

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of rates [42]. One can guess that very crucial here may be the packing of the chromophore intra the polymer matrices. Because this factor will determine the chromophore-polymer interchain interactions. Exciton diffusion determines and can be quantitatively related to the amount of exciton annihilation.

Bound polaron pairs possess a subpicosecond time scale and start to play an increasing role in the luminescence dynamics with enhancement of the decay of relaxed intra-chain excitons During the spin coating process the polymeric chains are prevalingly aligned in the plane of the substrate, and excitons migrate by inter-chain hopping in the direction perpendicular to the substrate. In the Ref. 43 it was established that intra-chain energy transfer is slower than inter-chain. Thus, we will deal three-dimensional anisotropy.

Following these evaluations one can expect that values of the chromophore ground state dipole moments should be crucial for the kinetics of excitons and of the free carriers.

As a confirmation from the table 1 one can see a good correlation between the values of the state dipole moments and the measured values of the open circuit voltage. This may reflect substantial role of the electron-phonon trapping polarized states in the processes of the charge separation for these types of the composites.

Table 1. Principal parameters of the PV.

Sequence of layers	V _{oc} [V]	I _{sc} [μA/cm ²]	FF	QE (%)	MD(D)	HOMO(eV)
Mol1+PDT	0.875	8.316	0.166	0,19	3.188	-8.39
Mol2+PDT	0.734	14.988	0.201	0.17	2.96	-8.57
Mol3+PDT	0.659	14.279	0.264	0,19	2.84	-8.53
Mol4+PDT	0.535	22.527	0.22	0,20	1.03	-8.13
Mol5+PDT	0.862	10.346	0.231	0,16	4.94	-8.31
Mol6+PDT	1,107	28,035	0,186	0,44	5.44	-8.33

In the Table 2 are presented the effective exciton radius calculated within the DFT B3LYP approach with taking into account of effective Coulombic dipole-dipole interactions calculated following the method similar to the described in the Ref. 44 .

Chromophore	Effective exciton diffusion length without inclusion of polaronic effects (nm)	Effective exciton diffusion length with inclusion of polaronic effects (nm)
Mol.1	7.6	7.4
Mol.2	7.85	7.61
Mol.3	7.7	7.52
Mol.4	7.2	7.01
Mol.5	8.4	8.11
Mol.6	5.6	5.37

Table 2.

. Generally the calculations determine an average radius of exciton which are inversely proportional to the excitonic binding energy. These states were calculated similarly to the method described in the Ref. 45. during calculations of the intermolecular excitons (so-called Davydow splitting). One can see that the exciton radius due to polaronic effects due to scattering on vibrational sub-levels are additional factors decreasing the effective exciton lengths. Moreover, one can see a better correlation between the exciton radius and the PV efficiencies with respect of a case of the state dipole moments. It is principal that the stability of the obtained parameters is saved more than 6 months,

5.CONCLUSIONS

We have established that introduction of polarizable cyano groups to the pyrazoloquinoline chromophore molecule leads to the enhanced state dipole moments. Such modification leads to the enhancement of the open circuit voltage up to 1 V. Some differences exist for the sample 4 which may reflect a deviation in the positions of the HOMO levels. Surprisingly, it is no obvious correlation between the short current and the state dipole moments or position of the HOMO levels of chromophore. Comparing to the PAQ chromophore without the cyano

substituent addition one can see that the values of the open circuit voltages are at least two times larger. In our case we deal with hole transport materials (PDT and PQDs). These compounds are likely donor materials. As a consequence there is not donor-acceptor interface for charge separation and it may be difficult to perform separation of hole-electron pairs for charge carrier generation. Moreover, if even the electron-hole pairs may be separated, it is also difficult to transport electrons to the electrode. For the such kinds of materials the only explanation may be given within the polaron mechanisms described within the electron-phonon coupling.

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MOL1

MOL2

MOL3

MOL4

MOL5

MOL6

PDT

Fig.1. Chemical structure of : MOL1-1,3-diphenyl-6-CN-1*H*-pyrazolo[3,4-*b*]quinoline, MOL2-1,3-dimethyl-6-CN-1*H*-pyrazolo[3,4-*b*]quinoline, MOL3-1-phenyl-3-methyl-6-CN-1*H*-pyrazolo[3,4-*b*]quinoline, MOL4- 1- methyl -3 phenyl -1*H*-pyrazolo[3,4-*b*]quinoline, MOL 5 - 6-*N,N*-Dimethylamino-1-(*p*-cyanophenyl)-3-phenyl-1*H*-pyrazolo[3,4-*b*]quinoline, MOL6- 6-*N,N*-Dimethylamino-3-(*p*-cyanophenyl)-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoline, PDT poly(3-decylthiophene-2,5-diyl), regioregular

Fig. 2. I-V characteristics under illumination of ITO/PDT+MOL / Al devices
 $P_{\text{light}} = 1315 \mu\text{W}/\text{cm}^2$ light.

Fig.3.I-V characteristics under illumination of ITO/active layer / Al devices
 $P_{\text{light}}=1315\mu\text{W}/\text{cm}^2$ light.

Fig. 4. Dependence of the open circuit voltage on the state dipole moments of the separate chromophore

Fig. 5 . Principal architecture of the photovoltaic cell.

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