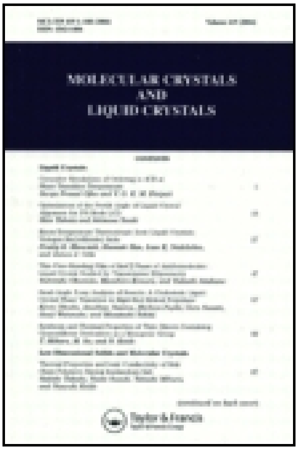

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Effect of the Controllable Molecular Ordering in a New Polymer on Carrier Transport and Photovoltaic Properties

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The functionalized soluble poly(p-phenylene vinylene) derivative bearing polar molecules (NLO-PPV) was designed and synthesized to investigate effects of molecular orientation in single-layer polymer photovoltaic devices. The active molecule is the 4-(N-butyl-N-2-hydroxyethyl)-1-nitro-benzene group on the copolymer. The grafting of the molecule with a donor/transmitter/acceptor structure, possessing a large ground state dipole moment, enables their orientation by a DC-electric field. An internal electric field in such layer facilitates exciton dissociation and improves charge transport. We report increase of the external quantum efficiency by a factor of 1.5 to 2 upon orientation. The associated effects on the carrier injection and transport depending on the orientation direction were evidenced.

Keywords: energy conversion efficiency; molecular orientation; optical and electrical properties; polymers

PACS numbers: 73.50.-h, 81.40.Rs, 81.40.Tv, 73.61.Ph

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1. INTRODUCTION

Photovoltaics (PV) is one of the up-and-coming sustainable energy sources for the future. Organic solar cells might promise a significant cost reduction for photovoltaic energy conversion if improvements of the power efficiency and the lifetime can be achieved. Though there still are some crucial obstacles to overcome before large-scale production of plastic solar cells can be considered, but the fast progress of this technology is encouraging [1,2,3]. In addition to the incorporation of polymers with improved light harvesting and charge transport properties, breakdown may come from the development of innovative concepts. A good illustration is the well-known interpenetrated network of acceptor type molecules with donor-type conjugated polymers which demonstrated the highest efficiencies in polymer based solar cells [4]. In this case, the significant improvement of the efficiency is due to the distribution of the exciton dissociating sites throughout the material volume. However, one of the main drawbacks remains the relatively low mobilities inherent to organic materials, which impose limitations of charge collection even in thin (usually less than 200 nm) PV devices. In this context, a promising approach could be based on the orientation of polar molecules incorporated in an amorphous polymer [5]. Because of orientation a rectifying junction over the whole single layer thickness could be realised, necessary to effectively dissociate photogenerated excitons and transport the created charge carriers. In this way a built-in internal field is induced in the structure, which therefore starts behaving as a homojunction distributed over the entire thickness of the device [5,6]. First experiments were performed on a copolymer of poly(methyl methacrylate) (PMMA) with Disperse Red 1 (DR1) (4-(N-(2-hydroxymethyl)-N-ethyl)-amino-4′-nitroazobenzene), as a polar molecule, covalently bound to the polymer chains. Orientation of the polar molecules, also called push-pull molecules used in second-order nonlinear optics [7], was achieved by application of a static electric field through the polymer film, while heating it near the glass transition temperature. Experimentally it was demonstrated that the current-voltage characteristics of a device made of this copolymer film sandwiched between symmetric electrodes become strongly asymmetric [8] upon orientation of the DR1. It was also demonstrated by time of flight (TOF) experiments that the molecular orientation causes the charge mobility to grow, meanwhile the barrier height between the electrode and polymer decreases [5]. The influence of molecular orientation on carrier transport and trapping effects was confirmed in the blends of poly(9-vinylcarbazole) (PVK) with 30% wt of diode-like 4-dibutylamino-4′-nitrostilbene

(DBANS) molecules by Thermally Stimulated Currents (TSC) and Current-Voltage (IV) characteristics [9]. The potential of the Solid Electric Field Induced Second Harmonic Generation (SEFISHG) method [10] has been employed to evaluate the internal field stored in the structure after the orientation of polar molecules [9]. On the other hand, optical depoling, first observed with an azo dye [11], is an important drawback in this approach, as it was observed also in molecules which don't exhibit trans-cis izomerization [12]. Therefore our idea was to investigate chemically grafted polar molecules instead of using their blends. The improvement of the efficiency of photovoltaic cells based on a single polymer layer bearing oriented polar chromophores was also clearly evidenced [6] although materials used in this study were not optimized for device efficiency. In this paper, we present the results obtained on a functionalised soluble PPV grafted with push-pull like molecules specifically developed to investigate the molecular orientation concept for photovoltaic applications.

2. SAMPLE PREPARATION AND EXPERIMENT

The functionalized soluble poly(*p*-phenylene vinylene) derivative bearing polar molecules (NLO-PPV) was designed and synthesized to investigate effects of molecular orientation in single-layer polymer photovoltaic devices. Chemical structure of the material is presented in Fig. 1. The synthesis route will be described in detail elsewhere. The active polar molecule is the 4-(N-butyl-N-2-hydroxyethyl)-1-nitro-benzene group on the copolymer. It is a typical push-pull molecule with a donor/transmitter/acceptor structure, possessing a large ground state dipole momentum which is necessary for the efficient DC-field orientation. Moreover, this grafted dye polar molecule presents no photoinduced molecular movements avoiding that

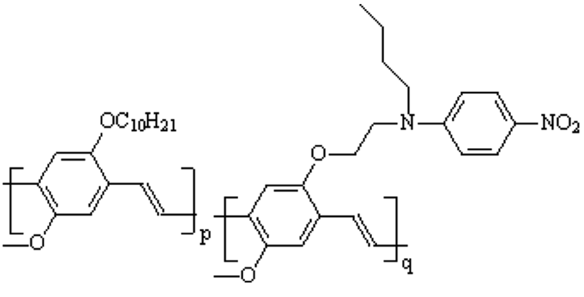

FIGURE 1 Chemical structure of the synthesized soluble NLO-PPV copolymer.

way disorientation caused by the solar light illumination. It was not the case of the DR1 previously used in a model system. The active molecule is attached onto a soluble poly(*p*-phenylene vinylene) (PPV) copolymer containing 50% of MDMO-PPV units. This copolymer is used as an isotropic polymer binder as MDMO-PPV is one of the best conjugated polymer systems so far leading to high solar efficiency. The resulting copolymer (NLO-PPV) contains 50%-molar chromophore concentration. Test devices with the thicknesses of the active layers between 55 and 80 nm were fabricated on the ITO-coated glass substrates. The copolymer film was spin-coated from a chlorobenzene solution. The semi-transparent Aluminium electrode was evaporated on the top.

Orientation of the polar molecules is achieved by application of the DC voltage between the electrodes of the device preheated close to its glass transition temperature T_g. The reverse bias was used to create polarization field oriented in the forward direction and vice versa. Afterwards, in order to freeze the molecular order, samples were cooled down to room temperature while maintaining the voltage. The T_g of this new polymer has been evaluated *in situ* by the Second Harmonic Generation (SHG) measurements. SHG enables evaluation of the molecular order $\langle \cos^3 \theta \rangle$ [13], the average polar orientation along the field direction, allowing thus optimization of the poling parameters: orientation field, poling temperature and duration. The T_g is found to be close to 55°C. Voltages of up to 100 V/μm were applied at this temperature for 10 minutes to create the orientation. The described orientation effects were reversible and reproducible after several orientation and disorientation cycles.

3. RESULTS AND DISCUSSION

3.1. Light Absorption Properties

The orientation of polar molecules is evidenced by the absorption spectra presented in Figure 2. The spectra were measured using illumination by the unpolarised light falling onto the sample surface at the normal incidence angle. It can be seen that the orientation of the polar molecules results in the decrease of absorption at 400 nm, wavelength of the absorption maximum related with the polar molecules. This can be reasonably explained by the orientation of the polar molecules perpendicularly to the polymer surface.

3.2. Current-Voltage Dependencies

Electrical characteristics of the test devices have been monitored in the dark. Though owing to the small polymer layer thickness, some

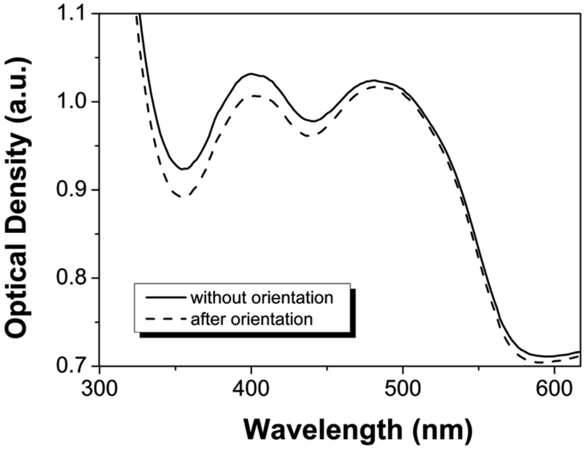

FIGURE 2 Absorption spectra of the device without orientation and after the orientation in forward direction.

prepared samples initially exhibited short circuits, usually they were readily cured during monitoring of the current-voltage (IV) characteristics. After that, all the samples from the same batch gave identical and reproducible results.

IV dependencies of a typical device are shown in Fig. 3. During the experiments, ITO electrodes were grounded, and voltage was applied to the Al electrodes. Behaviour of the IV curves was found to be dependent on the polarity of the orientation voltage, as it demonstrated in Figure 3. Usually orientation in the forward direction resulted in the increase of the current by up to one order of magnitude. In contrary, polarization with negative voltage leads at low biases to the decrease of the current as compared to the unoriented sample. This situation can be observed in Fig. 3 at applied voltages of up to 1 V. At higher voltages both currents measured after the orientation were higher than the current without orientation. Characteristically these changes were reversible after several polarization-depolarization thermal cycles with and without applied polarizing biases at high temperature, respectively.

3.3. Carrier Mobility

Carrier mobility behaviour depending on the orientation and applied electric field strength was investigated by the Charge Extraction by Linearly Increasing Voltage (CELIV) method [14,15]. The

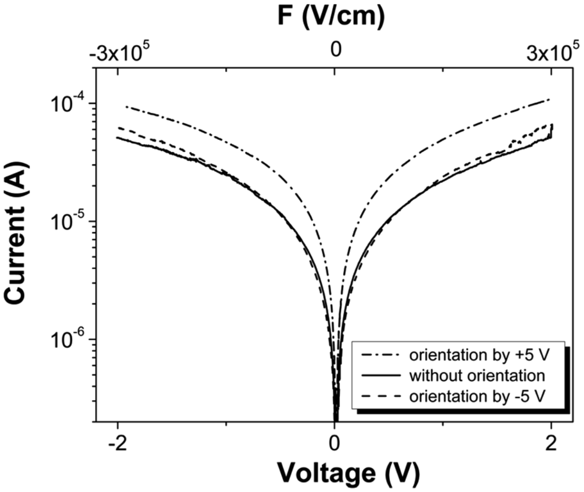

FIGURE 3 IV characteristics of the device without orientation and after the orientations in different directions.

experimental mobility dependencies are presented in Fig. 4(a). Characteristically, the biggest mobility differences are observed at lowest electric fields, depending on the polarization direction, i.e., polarity of the bias, used for the poling. A notable decrease of mobility takes place upon orientation of the polar molecules in the reverse direction, and, conversely, mobility increase is observed upon orientation in forward direction.

With increasing electric field strength mobility differences diminish. This can be explained by the fact that usually only a part of molecules are oriented, as, *e.g.*, it was also pointed out in [16]. In this reference authors report that in the DR1-MMA 35/65 system an effective degree of orientation of up to 30% could be reached. Therefore at higher applied electric fields the limited built-in polarization field cannot effectively influence carrier transport any longer, and the usual transport phenomena in inhomogeneous polymer matrix become prevailing. In this region a slight decrease of mobility takes place with increasing electric field (the so called “negative” mobility dependence). Within the framework of the Gaussian disorder model [17] such behaviour is characteristic for the spatially inhomogeneous systems.

By TOF similar effect was experimentally confirmed many times in different disordered materials as, *e.g.*, molecularly doped polymers, molecular glasses, etc. Though it was argued in [18] that sometimes TOF may give an erroneous overestimation of the mobility values if

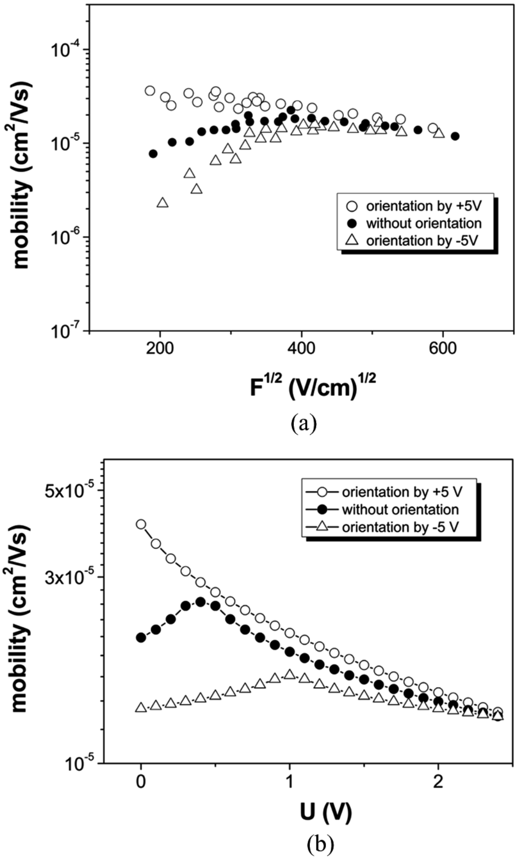

FIGURE 4 Effect of the molecular orientation on the mobility dependencies *vs* applied electric field strength. (a) – experimental data, (b) – modelling results.

the dielectric relaxation time τ_σ is shorter than the carrier transit time t_{tr}. The condition $\tau_\sigma > t_{\mathrm{tr}}$ has to be fulfilled in TOF to assure the constant electric field in a sample over its thickness (otherwise it can be redistributed by equilibrium charge carriers in time intervals shorter than t_{tr}), and to keep carrier number constant preventing them from recombination during their transit through the sample. The CELIV method was proved to be free of these limitations, and therefore to be much better suitable for the investigation of the high conductivity materials, in which enough carriers exist to create a measurable current upon extraction. In polymers, the negative mobility behaviour was first evidenced by CELIV in P3HT in [19] and P3OT in [20].

In our case, we had observed an unusual behaviour of the mobility with increasing external electric field that was especially well pronounced upon orientation in reverse direction: at the lowest fields mobility used to increase, reaching its maximum, and started decreasing again. To our knowledge such behaviour was never observed before. We have modelled it (Fig. 4b) using the Gaussian Disorder Model (GDM) [17]:

$$\mu(F,T) = \mu_\infty \exp\left[-\left(\frac{2\sigma}{3kT}\right)^2\right] \exp\left\{C\left[\left(\frac{\sigma}{kT}\right)^2 - \Sigma^2\right]\sqrt{F}\right\}. \tag{1}$$

This equation was derived from Monte-Carlo simulations of the hopping processes of charge carriers in a material with energetic (σ) and positional disorder (Σ) described by the Gaussian distribution functions. In this equation F is the electric field strength, μ_∞ is the high temperature limit of the mobility and C is a specific parameter that is obtained from the simulations as $C = 2.9 \times 10^{-4}\,(\mathrm{cm/V})^{1/2}$. To model the experimental behaviour of mobility we took into account the superposition of three electric fields present in the system:

$$\vec{F} = \vec{F}_{cont} + \vec{F}_{orient} + \vec{F}_{ext}. \tag{2}$$

Here $\vec{F}_{cont}$ is the built-in contact field given by the different workfunctions of Al and ITO, $\vec{F}_{orient}$ is the orientation-induced internal field and $\vec{F}_{ext}$ is the applied external field. The observed maximum can appear in the system in which mobility diminishes with increasing resulting electric field strength.

Characteristically, dependence of mobility on the molecular orientation at lower electric fields of up to $(1 \div 1.5) \times 10^5$ V/cm qualitatively coincides with the described behaviour of the IV curves. Such results enable one to state that in this region mobility makes a primary influence on the current. On the other hand, big differences in current at higher fields depicted in Fig. 3 cannot be attributed to the mobility, which becomes independent on the polarization. Probably modification of contact or surface effects cannot be excluded in this case, but this requires further investigation.

Moreover, though the qualitative agreement of the experimental and model data is quite good and explains appearance of the mobility maximum, the exact fitting using the simple approach was not possible. This could be because of the non-constant electric field strength over the thickness of the layer. Furthermore, within the framework of GDM, polarization by -5 V, leading to the appearance of the built-in field in reverse direction, could cause mobility drop because of the increased energetic and/or spatial disorder in the material. Indeed, one can assume that partial orientation of molecular dipoles in reverse direction might introduce more energetically and/or spatially scattered transport and/or trapping states that disturb carrier movement, i.e., their hopping between allowed states because of their trapping. In contrast, if the polar molecules become oriented by +5 V to create the built-in field in the forward direction, the energetic disorder is reduced and mobility behaviour is governed by the positional disorder according, resulting in the "negative" mobility behaviour, as discussed above.

3.4. External Quantum Efficiency

External Quantum Efficiency (EQE) measurements of the samples were performed before and after the orientation with different voltages by illumination either through the ITO electrode or through the Al electrode. Results are presented in Fig. 5. The EQE are dependent on the orientation direction in the whole spectral region. For the orientation in forward direction we have observed an overall increase of the photogenerated current, while in the case of the negative bias a decrease took place. The observed effect is not due to a purely optical modification, as, *e.g.*, variation of the optical density, described above and presented in Fig. 2, since the EQE increase occurs over the whole spectrum. Moreover, these observations are consistent with the IV and mobility data obtained at lower fields. Qualitative effect of the

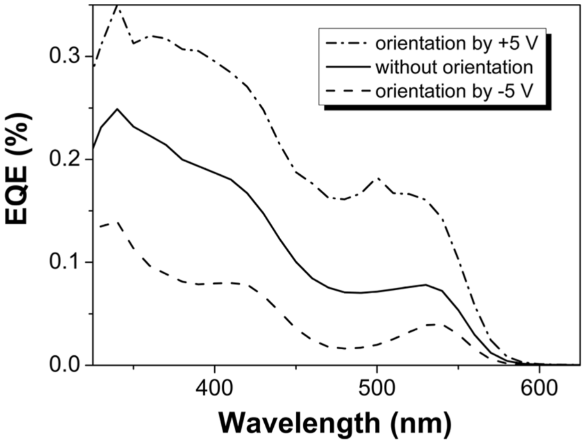

FIGURE 5 External quantum efficiency spectra measured for different orientation field directions.

orientation direction is similar, confirming the role of carrier transport. The conditions for the carriers to move are improved after the orientation in forward direction and carrier transport is aggravated after the orientation in reverse direction as compared to the unoriented sample. An increase of the EQE by a factor of 1.5–2 could be evaluated by integrating the photocurrent over the visible region after the orientation by positive bias as compared to the unoriented device.

In the tested devices EQE remains relatively low as compared to the characteristics of the photovoltaic solar cells made on the MDMO-PPV basis. However, this is not surprising, since the test devices were not optimised in terms of the absorption and charge collection efficiency by the electrodes. Further optimisation will also be related to the determination of the optimum grafting rate of the polar molecules, what will require modelling of the internal field that could be stored in the device.

4. SUMMARY AND CONCLUSIONS

We report investigations of the new purposefully designed and synthesized functionalized soluble poly(*p*-phenylene vinylene) (PPV) derivative bearing push-pull like molecules (NLO-PPV). The grafting of the push-pull molecule with a donor/transmitter/acceptor structure, possessing a large ground state dipole momentum, enables the efficient molecular orientation by a DC-electric field. The NLO-PPV thin film samples with thicknesses between 55 and 80 nm were produced by the spin coating on ITO glass. Semi-transparent Al contacts were evaporated on the top. The molecular orientation was achieved by application of the constant external electric field, up to 100 V/μm, at the temperature near the copolymer glass transition temperature of about 55°C. The reverse bias was used to create polarization field oriented in the forward direction and vice versa. The effect of orientation on the carrier injection and transport properties depending on the polar molecules orientation direction was evidenced by the Current-Voltage characteristics and mobility measurements using the Charge Extraction by Linearly Increasing Voltage method. We demonstrate increase of the external quantum efficiency by the factor of up to 1.5–2. To our knowledge this is the first experimental demonstration of the improvement of external quantum efficiency of photovoltaic device induced by the orientation of the polar molecules contained inside the active layer. This improvement is associated with the growth of the mobility, resulting also in the increase of the device current. In contrast, orientation in the reverse direction resulted in the drop of mobility, device current and external quantum efficiency.

These effects were reversible and repeatable during the orientation and disorientation cycles of the polar molecules by heat treatment.

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