# ADVANCED MATERIALS Communications Molecular Rectification in Oriented Polymer Structures""

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# Molecular Rectification in Oriented Polymer Structures**

By *Carole Sentein,* *Céline Fiorini, André Lorin,* and *Jean-Michel Nunzi*

Polymeric semiconductor devices are receiving increasing attention in view of potential applications requiring low-cost processing over large areas.[1,2] In this respect, unlike with evaporated molecules, the wet-processing capability of polymers offers total compatibility with other complementary technologies. The concepts from which organic-semiconductor devices are designed are mostly derived from inorganic-semiconductor physics and technology.[3]

In order to build efficient organic-semiconductor devices such as electroluminescent or photovoltaic solar cells, a rectifying junction is required. Such junction can be of two main types:[4] Schottky junctions between an organic semiconductor and a metal, and p-n junctions between two p- and n-type organic-semiconductors. The Schottky junctions often suffer from degradation problems originating from electrochemical potential differences at the rectifying contacts, which induce diffusion of electrode material into the polymer.[5] Such a drawback is corrected with p-n junctions in which metal to polymer contacts are ohmic. However, p-n junctions require the use of two polymer layers with wet-processing compatibility. Moreover n-type organic-semiconductors are less common than p-type ones owing to their lower stability under oxygen which is a consequence of their reductive behavior.

We report here a different approach in which oriented diode-like molecules, the so-called push–pull molecules used in nonlinear optics,[6] are contained inside a polymer binder. Oriented molecules induce a rectifying effect, behaving as a distributed homojunction within a single polymer thin film. In order to demonstrate the principle, we start with an initially symmetric structure: the polymer film is sandwiched between two identical electrodes. The current–voltage characteristics of the device are also symmetrical. By application of a static electric field through the polymer film, while heating near the glass transition temperature $(T_g)$, dopant molecules are oriented in the field with an order parameter $\langle \cos\theta \rangle$.[7] The current–voltage characteristics then become strongly asymmetric.

Experimentally, molecular order is controlled using second harmonic generation (SHG): it appears that SHG-in-

tensity is related to the induced rectification behavior. The principle we demonstrate relies on the intrinsic polar nature of organic molecules. It cannot be readily applied to inorganic semiconductors which are built from spherical atoms; polarity being a crystal-cell property. Time of flight (TOF) experiments reveal an unipolar increase of the electron mobility through orientation, thus confirming the molecular-diode organization effect. This new type of junction is expected to improve significantly the efficiency of polymeric semiconductor devices.

Figure 1 presents the current–voltage characteristics of the symmetric-electrode device monitored before and after orientation under different strengths of orientation-field. The rectifying effect induced by molecular orientation in the symmetric-electrode device is clearly seen in Figure 1, for orientation voltages larger than 10 V. It
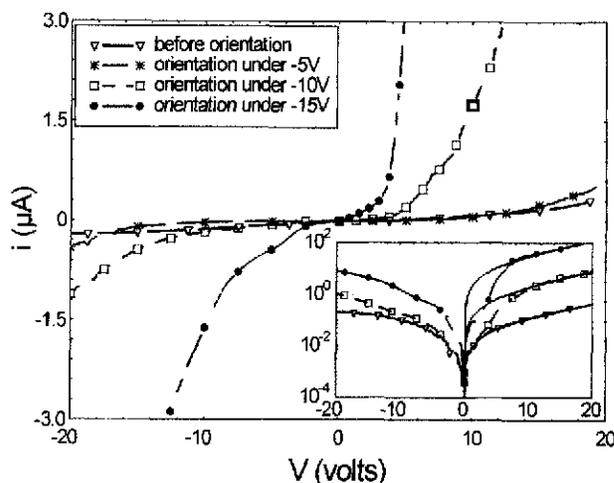


Fig 1. Current–voltage characteristics of the Al/copolymer/Al symmetric device before and after orientation by different voltages. Data markers are used as a guide to the eye. The insert is the absolute value of measured current in a logarithmic scale. In the insert continuous lines show fits of the Schottky model for the positive parts of I–V curves.

corresponds to an orientation field close to 100 V/μm. The insert in a logarithmic scale clearly shows that there is no initial rectification in the non-oriented device. The same effect was observed using symmetric-ITO electrodes instead of aluminum. This proves that rectification is not due to some interfacial effect occurring between polymer and electrodes, such as aluminum oxidation.

In contrast, no rectification is induced using a single PVK-polymer film. This proves that rectification is not related to charge trapping effects. No more rectification is induced in a 30 wt.-% non-polar phthalocyanine–PMMA blend. On the other hand, we replaced Disperse Red (DR1) by *N*-dibutyl-4-amino-4'-nitrostilbene (DBANS), another push-pull polar molecule, in a PVK-polymer blend. The induced rectification is then qualitatively the same as for DR1. This proves that internal rectification is typical of the orientation of polar molecules.

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The positive part of the current–voltage curves can be fitted using standard charge injection models.[3] In order to estimate the rectification behavior, we chose the Schottky diode model which describes successfully the vast majority of single layer organic-semiconductor devices probed under fields up to around 100 V/μm,[9,10] where $I$ is the measured current, $I_s$ the saturation current, $V$ the applied field, $n$ the so-called ideality factor, $q$ the electron charge, $k$ the Boltzmann constant and $T$ the absolute temperature.

$$I = I_s \left[ \exp\left(\frac{qV}{nkT}\right) - 1 \right] \qquad (1)$$

For each device orientation-field value, we get the saturation current. Using the usual analogy with inorganic semiconductors,[3] we then calculate the equivalent barrier height $\Phi_b$ between metal and polymer in the frame of the thermionic emission model, where $A$ is the diode area and $R^*$ is the so-called Richardson constant usually approximated to its free electron value of $120 \, A \, cm^{-2} \, K^{-2}$.

$$I_s = AR^*T^2 \exp\left(\frac{-q\Phi_b}{kT}\right) \qquad (2)$$

In order to get a measurement of the molecular order $\langle\cos\theta\rangle$ the average polar orientation along the field direction, we performed second-harmonic generation experiments.[7] Initially, polar molecules are distributed isotropically, the material is centrosymmetric, and no SHG signal is detected. During the orientation step, we monitored the increase of the SHG signal, which is proportional to the square of the molecular order $\langle\cos\theta\rangle$ (insert in Fig. 2).[6,7] SHG-monitoring permits optimization of the sample orientation parameters, i.e., orientation field, sample temperature, poling duration, and cooling conditions, in order to achieve the largest stable orientation.

Experiments were performed using a picosecond Nd:YAG laser. Using the same symmetrical device (Al/DR1-MMA-50/50 copolymer/Al) as the one used for the determination of the current–voltage characteristics in Figure 1, SHG was measured for each orientation field value. SHG was monitored before and after $I$–$V$-characteristic recording, without any change, indicating that molecular order is frozen despite the large fields achieved. Moreover, we performed SHG at ambient temperature in fields up to 220 V/μm, without any permanent SHG variation.

The relationship between the equivalent barrier height $\Phi_b$ and molecular order $\langle\cos\theta\rangle$ is shown in Figure 2. Through molecular orientation, we achieve a 0.2 eV reduction in the equivalent barrier height, $\Phi_b$, which is a measure of the induced internal rectification, exhibits a quasi-linear experimental dependence with molecular order. This phenomenological dependence may be attributed to the storage of an internal polarization field proportional to $\langle\cos\theta\rangle$.

Together with the asymmetry of the $I$–$V$ curve induced upon orientation in Figure 1, molecular-diode organization may affect charge mobility. In order to address this point, we performed time of flight (TOF) experiments.[11] Samples used for TOF were 1.5 μm-thick films sandwiched between a transparent ITO-electrode and an Al-electrode. A typical TOF transient obtained with the strongly absorbed frequency-doubled output of a pulsed Nd:YAG-laser is given in the insert of Figure 3. Majority carriers in the DR1-
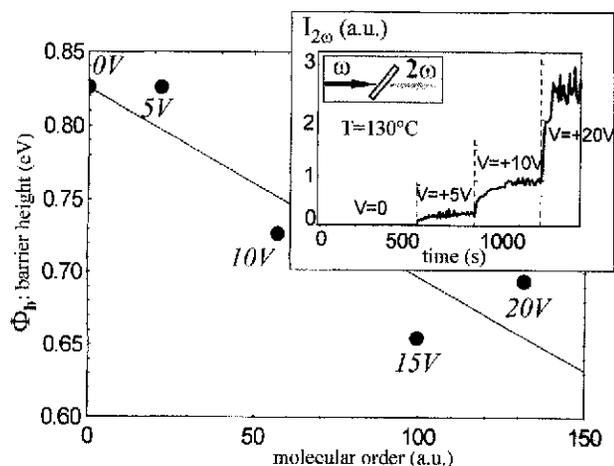
Fig. 2. Variation of the equivalent barrier height between Al and DR1-MMA-50/50 copolymer with respect to the DR1-molecules orientation order in the PMMA matrix. Molecular order is given as the square root of SHG-signal. Barrier height $\Phi_b$ is deduced from current–voltage characteristics. Insert depicts SHG-growth with time at 130°C under different orientation-field values.
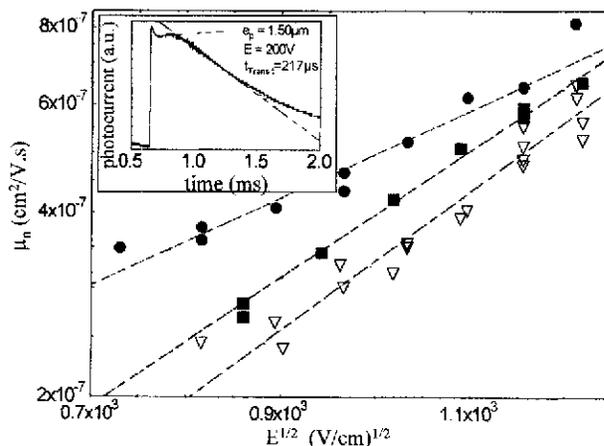
Fig. 3. Field dependence of the electron drift-mobility in the DR1-MMA-50/50 copolymer before orientation (open triangles), after direct orientation under 100 V (full squares), and after reverse orientation under –100 V (full circles). Insert depicts a typical TOF transient for the unoriented sample.

MMA-50/50 copolymer appear experimentally to be electrons. Field-dependence of the electron drift-mobility is given in Figure 3, before orientation and after orientation with two opposite orientation-field values. The mobility exhibits a Poole–Frenkel-type field dependence.[11]

The increase of the electron mobility is significant when molecules are oriented under reverse bias with respect to

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the measurement field; that is to say with the acceptor group oriented towards the Al-electrode. On the other hand, mobility is weakly changed when molecules are oriented under direct bias. By extrapolation to its zero-field limit using the Poole–Frenkel dependence, mobility in the sample oriented under reverse bias is increased by a factor of 4 with respect to the unoriented sample. According to Figure 2, the internal field resulting from molecular orientation is close to 2 V/μm ($\Delta\Phi_b \approx 0.2$ eV in a 130 nm thick device): it is negligible compared to the field applied for mobility measurements (Fig. 3). As a consequence, unipolar enhancement of the mobility reveals the molecular-diode organization effect through orientation.

In conclusion, we have given experimental evidence for molecular rectification in an oriented amorphous polymer incorporating polar chromophores. Rectification implies storage of an internal field, thus reducing potential barriers for charge injection or extraction at both electrodes. Reduction of potential barriers may slow down oxidation–reduction reactions occurring spontaneously at non-ohmic metal–polymer junctions, thus slowing down device degradation. Additionally, using engineered asymmetric electrodes, this rectification effect may improve significantly the efficiency of polymeric semiconductor devices such as photovoltaic cells and electroluminescent diodes. Polar organization of molecular diodes is equivalent to the build-up of a distributed p-n homojunction within a single polymer film. In addition to the ease of processing of such devices, our solution offers a crucial advantage over usual p-n junctions. The efficiency of organic-semiconductor p-n junction devices is usually limited by the weak extension of the depletion zone (typically 10 to 50 nm),[4] in which the majority of charge separation or recombination processes take place. Our solution provides a depletion zone extending over the whole polymer film thickness. Moreover, diode-like molecules orientation results in an enhancement of charge mobility. This may also improve organic-device efficiency which suffer from low charge mobilities.

The materials used in this study have not been optimized for device efficiency, but rather they were designed in order to demonstrate rectification induced through orientation of diode-like molecules. An optimization route with respect to long-term stability would consist in designing a high-$T_g$ semiconducting polymer. Additionally, the poling technique may be greatly improved by using the corona-poling technique[6] which permits the achievement of larger orientation orders over large areas. Experiments are now in progress to apply this principle to photovoltaic solar cells.

## Experimental

As an active polar molecule, we used Disperse Red 1 (DR1): 4-(N-(2-hydroxyethyl)-N-ethyl)-amino-4'-nitroazobenzene. It is a typical push-pull molecule with a donor/transmitter/acceptor structure and it possesses a large ground state dipole moment μ which is necessary for efficient DC-field orientation. It is attached onto polymethylmethacrylate (PMMA) which is

used as an isotropic polymer binder. The resulting copolymer DR1-MMA-50/50 contains 50 %-molar chromophore concentration [8]. Its glass transition temperature is $T_g = 132$ °C.

Test devices were realized on top of standard glass slides. They consisted of a vacuum-evaporated 12 nm-semi-transparent aluminum bottom-electrode, covered by a 130 nm DR1-MMA-50/50 copolymer film spin-coated from a 1,1,2-trichloroethane solution, and finally recovered by a second identical semi-transparent aluminum top-electrode. The active surface of the device was 26 mm².

Orientation of the polar molecules was achieved by application of a 5 to 20 V voltage between the electrodes for 10 min while the device was heated at 130 °C. The sample is then cooled down to room temperature with the voltage still applied, in order to freeze-in the molecular order. 80 % of the molecules remain oriented after more than two months. Owing to the small polymer-film thickness, some samples prepared in this way initially exhibited short circuits. These short-circuits were readily cured during monitoring of the very first current voltage characteristics. After curing, all the samples from the same batch gave identical and reproducible results. The preparation technique also was reproducible.

[1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burn, A. B. Holmes, *Nature* 1990, *347*, 539.
[2] G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, A. J. Heeger, *Nature* 1992, *357*, 477.
[3] S. M. Sze, in *Semiconductor Devices: Physics and Technology*, Wiley, New York 1985.
[4] D. Wöhrle, D. Meissner, *Adv. Mater.* 1991, *3*, 129.
[5] E. Gautier, A. Lorin, J. M. Nunzi, A. Schalchli, J. J. Benattar, D. Vital, *Appl. Phys. Lett.* 1996, *69*, 1071.
[6] C. Bosshard, K. Sutter, P. Prêtre, J. Hulliger, M. Flörsheimer, P. Kaatz, P. Günter, in *Organic Nonlinear Optical Materials 1*, Gordon and Breach, London 1995.
[7] K. D. Singer, M. G. Kuzyk, J.E. Sohn, *J. Opt. Soc. Am. B* 1987, *4*, 968.
[8] D. Broussoux, F. Chastaing, S. Esselin, P. Le Barny, P. Robin, Y. Bourdin, J. P. Pocholle, J. Raffy, *Rev. Tech. Thomson-CSF* 1989, *20–21*, 151.
[9] J. K. Jeszka, *Mater. Sci. Forum* 1995, *191*, 141.
[10] M. Sprave, R. Blum, M. Eich, *Appl. Phys. Lett.* 1996, *69*, 2962.
[11] W. D. Gill, in *Photoconductivity and Related Phenomena* (Eds: J. Mort, D. M. Pai), 1976, Ch. 8.

## Mesoporous Silica with Micrometer-Scale Designs**

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The decoration of surfaces by ultraviolet and X-radiation, ion and electron beams,[1] microcontact printing, micromachining and lithographic molding technologies,[2] provides patterned structures of sub-micrometer dimen-

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