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A Molecular Photosensor Based on Photoswitching of Charge Carrier Mobility

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Summary: Polymer photoelectronic device based on interaction between π-conjugated polymer matrices and photochromic molecules was fabricated. The theoretical and experimental studies proved that the photochromic reaction in studied devices should eventuate in changes of optical and electrical properties of polymers such as luminescence and conductivity. The quantum chemical calculations showed that the presence of dipolar species in the vicinity of a polymer chain modifies the on-chain site energies and consequently increases the width of the distribution of hopping transport states. Optical switching was studied using standard absorption and photoluminescence spectroscopy. A strong photoluminescence quenching after the photochromic conversion caused by radiative energy transfer was observed. The influence of photoswitchable charge carrier traps on charge transport were evaluated by Space Charge Limited Current (SCLC) method. It was shown that deep traps may significantly affect the energy of the transport level, and thus modulate the transport of charge carriers.

Keywords: charge transport; conjugated polymers; quantum chemistry

Introduction

Polymer materials are poised as never before to transform the world of circuit and display technology. Nowadays, various polymers and polymer composites are used in xerography and laser printers, electroluminescent diodes and flat displays, the functional polymers are applied even in the logical circuits, which give rise to a new branch – 'Plastic Logic'. Multistable molecular systems attract much attention because of their potential use in optical and electro-optic devices such as broadband optical modulators, holographic and image forming media, rectifiers, sensors and switching devices.[1–3] New polymer materials are able not only to substitute the expensive crystalline semiconductors in these devices, but their specific properties originate the essentially new devices and technologies.

Due to their electronic structure, π-conjugated polymers are one of the most utilized materials in organic optoelectronic devices. The essential property which comes out from conjugation is that the π-electrons are much more mobile than the σ-electrons; they can jump from site to site between carbon atoms with a low potential energy barrier as compared to the ionization potential. The π-electron system has all the essential electronic features of organic materials: light absorption and emission, charge generation and transport.

As the conductivity mechanism in these materials, a variable-range hopping in a positionaly random and energetically disordered system of localized states is widely accepted.[4,5] Over the last decades, hopping in random systems was extensively

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studied. Among these studies, the approach based on so-called effective transport energy level was shown to be especially efficient.[6,7] When the effective transport energy is established, the variable range hopping problem is virtually reduced to trap controlled transport model. According to this model, the transport of charge carriers in molecular solids is strongly influenced by the presence of centres capable of localizing charge carriers (traps). It was shown that deep traps may significantly affect the energy of the transport level and mobility of charge carriers[8] and thus control their transport.

The molecular photosensor suggested in this paper is based on the control of charge carrier transport in π-conjugated polymers by photochromic additive. In a photochromic molecule the absorption of a light quantum leads to reversible conformational changes and the process follows displacements of the optical absorption bands. Examples of such photochromic molecules utilized in optical and optoelectronic switches are spiropyran and spirooxazine derivatives. In these materials a photochromic transformation between low and high energy state is accompanied by change of conjugation lengths resulting in control of the electronic structure along the molecule. The photochromic conversion can also results in the change of the dipole moment of the molecule, which consequently act as charge trap. This feature has been used in the design of a special type of optoelectrical sensor.

In our earlier papers[9–11] the concept of an electroactive molecular modulator was put forward. The molecular sensor should be based on the electronic function of a polymer matrix which contains photochromic groups able to modulate the transport of charge carriers. Guest molecules will in general have different energy levels from the host. In particular, if ionization energies and electron affinities are suitably different, charge carrier traps can be formed. A special type of traps may occur if guest molecules possess a permanent dipole moment. The dipole moment contributes to the field acting on surrounding molecules and shifts polymer transport levels. These dipolar traps are formed on neighbouring host molecules, even though the impurity itself does not necessarily form a chemical trap. For practical sensing applications, one can easy monitor either the steady-state or alternating conductivity of thin polymeric films prepared by low-cost manufacturing by common printing techniques.[12] In principle, the spectral and kinetic parameters of the sensor should be tuned by the selection of polymeric matrix and/or photochromic additive. The purpose of the present work is to examine by quantum chemistry modeling and experimental characterization the optical and electrical switching properties of the suggested sensor. For the study the π-conjugated photoconductive polymers poly[2-methoxy-5-(2′-ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV) and poly[(p-phenylenevinylene)-alt-(2-methoxy-5-(2′-ethylhexyloxy)- p-phenylenevinylene)] P(MEHPV-alt-PV) doped by photochromic spiropyran 6-nitro- 1′,3′,3′,-trimethylspiro[2*H*-1-benzopyran- 2,2′-indoline] (SP), which can be converted to a higher dipole moment possessing form referred to as (photo)merocyanine (MC), were used.

Theoretical Modeling

The presence of polar additives in the vicinity of a MEH-PPV chain modifies the polymer transport levels due to the charge–dipole interactions. MEH-PPV is a hole transporting material, hence the energy ε_n of a charge carrier located on an n-th repeating unit (phenylene or vinylene) is essentially equal to the negative of its first ionization potential I_n. For a doped polymer, the value of I_n is shifted by the sum of the electrostatic potentials describing the charge–dipole interactions of this charge carrier with all surrounding polar additive molecules. Since the positions and orientations of the additive with respect to the polymer chain are essentially random, this effect leads to an increase of the width $\sigma(\varepsilon)$

of distribution of hopping transport states (energetic disorder). If point dipoles are assumed, $\sigma(\varepsilon)$ is proportional to the additive dipole moment m, i.e. $\sigma_{MC}(\varepsilon)/\sigma_{SP}(\varepsilon) = m_{MC}/m_{SP}$. The dipole moments of SP and MC forms calculated by the Hartree-Fock method are 5.5 and 11.9 D, respectively. While the value obtained for SP is close to reality, the dipole moment of MC is probably underestimated since the polar environment increases the zwitterionic character of MC. Bletz et al.[13] reported the dipole moment of MC measured in a polar environment to amount to $15 \div 20$ D. For these reasons, one can expect two- or three-fold increase of the energetic disorder during the SP → MC reaction.

The influence of energetic disorder on the hole mobility was calculated by means of a tight-binding approximation model. The polymer chain is modeled by a sequence of $N = 4000$ sites corresponding to the repeating units (phenylenes and vinylenes). The hole motion on such a chain can be described by the Hamiltonian

$$H = \sum_{n=1}^{N} [\varepsilon_n a_n^{+} a_n - b_{n,n+1}(a_{n+1}^{+} a_n + a_n^{+} a_{n+1})], \tag{1}$$

where a_n and a_n^{+} are annihilation and creation operators of a hole at an n-th site, ε_n is the energy of a charge carrier localized at this site, and $b_{n,n+1}$ is the transfer integral between the sites n and $n+1$. Both quantities ε_n and $b_{n,n+1}$ are influenced by the random structure of the polymer chain and its surrounding. For transfer integrals $b_{n,n+1}$, the random distribution suggested by Grozema et al.[14] was used. In order to get the ε_n distribution, randomly oriented additive molecules, modeled as point dipoles, were randomly placed in the vicinity of the chain. It was assumed that no additive molecule was placed at a distance shorter than 10Å from the chain. This value was estimated from the chemical structures of the studied molecules. The concentration of the additive was taken to be $c = 4 \times 10^{-4}$Å^{-3}. For each repeating unit, ε_n was calculated as a sum of I_n and Coulombic electrostatic potentials from all additive molecules.

Using the Hamiltonian (1) with the molecular parameters ε_n and $\beta_{n,n+1}$ and the hole wave function $|\psi(t)\langle$ taken in the form of a linear combination of the states located at the individual sites, the time-dependent Schrödinger equation was numerically integrated. Getting the wave function in the site representation, it is easy to calculate the frequency dependent intramolecular ("on-chain") charge carrier mobility $\mu(\omega)$ by the well-known Kubo formula[15]

$$\mu(\omega) = \frac{-e\omega^2}{2k_B T}\mathrm{Re}\left[\int_0^\infty \Delta^2(t)\exp(-i\omega t)dt\right], \tag{2}$$

where e is the elementary charge, k_B is the Boltzmann constant, T is temperature, $\omega = 2\pi f$ is frequency of the external field, and $\Delta^2(t)$ is the mean-square displacement of the hole defined by the relation

$$\Delta^2(t) = \langle\psi(t)|n^2|\psi(t)\rangle\lambda^2, \tag{3}$$

where $\lambda = 3.35$ Å is the inter-unit distance.

The charge carrier mobility $\mu(\omega)$ calculated for the undoped polymer chain and the chains doped by additives with different dipole moments up to 12 D are shown in Figure 1. For $m > 12$ D the mobility $\mu(\omega)$ is so small that it is difficult to achieve the numerical stability. The presented data were obtained by averaging over 3000 realizations of the transfer integral and energetic disorder. The results show monotonic decrease of $\mu(\omega)$ with increasing m in the whole frequency range. The change of the additive dipole moment from ca. 6 D to 12 D (corresponding to the calculated change of the dipole moment during the studied photochromic reaction) should result in an almost five-fold decrease of the on-chain mobility. The effect would be even more pronounced if the experimental value of the MC dipole moment (≈18 D, see ref.[13]) is considered.

Although our simple model is neglecting several other effects like dynamical fluctua-

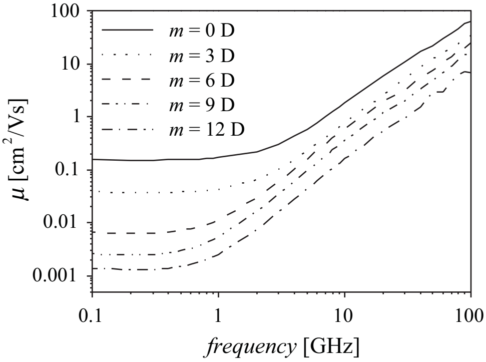

Figure 1.
The charge carrier mobility μ calculated for different additive dipole moments *m*. For frequencies lower than ca. 0.5 GHz mobility is almost frequency-independent because of the diffusive charge carrier motion.

tions of disorder or polaron formation that influence the mobility values, we believe the calculated mobility *ratio* is essentially correct, since the photochromic mobility switching arises from the change of the levels of the static disorder.

Experimental Part

Polymer devices were manufactured as a sandwich cell with a dielectric multilayer. Samples consisted of transparent indium tin oxide (ITO) electrode on a glass substrate on to which the 15 nm thin layer of poly(2,3-dihydrothieno-1,4-dioxin) (PEDOT) was spin cast from water solution to decrease the injection barrier for holes. Then, the active polymer layer, typically 150 nm thick, was spin coated from chloroform solutions of P(MEHPV-alt-PV) with $5 \div 30\%$ wt. of spiropyran. To decrease the contact injection barrier for electrons a thin 10 nm layer of Alq_3 (8-hydroxyquinoline, aluminium salt) was vacuum evaporated and the structure was completed by evaporation of aluminium top electrode 100 nm thick. Average device area was 3 mm^2.

The photochromic reaction of SP was activated using a mercury discharge lamp HBO 200 with band filter (360 ± 20) nm. Optical switching was studied using standard absorption and photoluminescence spectroscopy (PL). The electric response was studied by measuring the current-voltage (*I-V*) characteristics of the samples in the dark with Keithley 6517A electrometer.

Results and Discussion

The photochromic behaviour of spiropyran derivatives has been investigated by many researchers.[16–18] Under irradiation of an appropriate light energy, the spiropyran exhibits photochromism as shown in Figure 2. The photochromic reaction is accompanied by a charge redistribution resulting in a significant increase of the dipole moment of the molecule.

The studied spiropyran (SP) is stable in its colourless closed ring isomeric form, while UV irradiation produces a metastable open ring isomer (photo)merocyanine (MC) absorbing at 550–600 nm. The maximum of the absorption band of P(MEHP-V-alt-PV) is situated at 455 nm, the addition of SP increases the absorption of the sample in the UV region. Since the neat SP do not absorb in the VIS region, the absorbance of the doped samples is not affected by the presence of the SP molecules and can be seen in the top part of the Figure 3. The basic absorption spectra of the 30% mixtures and their relative changes after 1 minute illumination at 360 nm (conversion

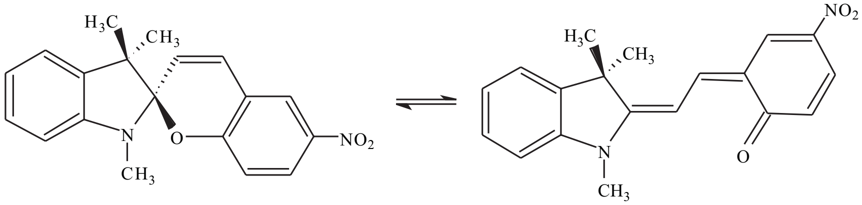

Figure 2.
Photochromism of the spiropyran molecule.

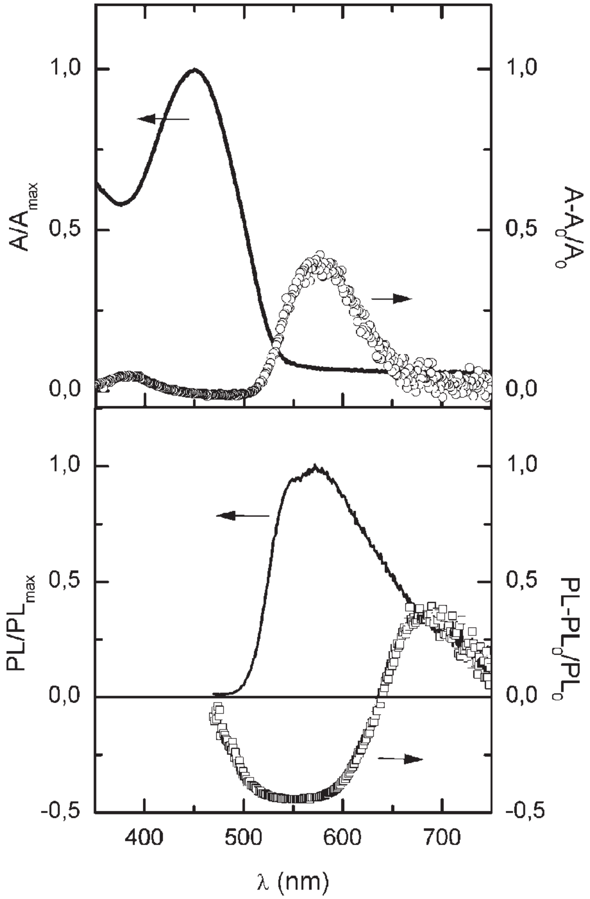

Figure 3.
Top: Normalised absorbance of P(MEHPV-alt-PV) with dispersed spiropyran (full line) and its relative change (scattered) after 1 minute illumination at 360 nm. New absorption band coming from the (photo)merocyanine (MC) can be observed. Bottom: Normalised photoluminescence (PL) of the P(MEHPV-alt-PV):SP mixture (full line). The scattered line represents a change in the spectrum after the MC formation. Decrease in the photoluminescence of the polymer accompanied by the formation of new band belonging to the MC can be observed. The excitation wavelength used was 455 nm. The energy was therefore absorbed by the P(MEHPV-alt-PV) and subsequently transferred to the MC molecules.

of SP to MC form) are also depicted in Figure 3. The photoinduced colour change of SP is caused by the extension of conjugation in the MC isomer compared to the orthogonal structure of the SP form.[19] Annealing in the dark or irradiation with a He-Ne laser gradually restores the original spectrum, the change being reversible.

Bottom graph of the Figure 3 shows the normalized photoluminescence (PL) spectra of P(MEHPV-alt-PV):SP mixtures and their relative changes after 1 minute illumination at 360 nm. The stable form of spiropyran (SP) does not show any luminescence contrary to its MC form. The polymer shows its own luminescence (Figure 3 bottom) and creation of MC form via the photochromic reaction therefore could result in the appearance of new PL bands. However, MC possesses a high dipole moment that generally causes quenching of luminescence. The quenching was found to be strong even in the case when the $SP \rightarrow MC$ conversion was very weak (sometimes not observable in absorption spectra, typically for <20% wt. doped samples). The intensity of the quenching was proportional to the amount of the SP. Generally, the efficiency of the photochromic conversion was found rather low in these systems. This is probably due to a competition between the absorption of the UV light used to activate the photochromic conversion of the photochromic system and the polymer matrix. Inner filter effect can also play a significant role. For that reason only the 30% system is discussed. Furthermore, excitation at 455 nm (polymer absorption) led to a noticeable luminescence at 660 nm (coming from MC). The energy absorbed by P(MEHPV-alt-PV) was hence transferred to MC and radiative decay was observed. Since the polymers used are good photoconductors, the energy transfer is competitive to the creation of free charges which give rise to the photocurrent. The drop of the polymer photoconductivity was characterised by impedance spectroscopy.[20] After the reverse $(MC \rightarrow SP)$ reaction was completed, the polymer PL was recovered, the reversibility of the process was, however, unsatisfactory because of a strong photodegradation of the polymer matrices. Study of degradation processes by absorption and PL spectroscopy shows blue shift of the maximums. In energetically disordered systems the preferential bleaching of energetically lower lying sites means good migration of excitons. For further details on the optical characterization of the spiropyran photochromic reaction in conjugated polymeric environment see our previous work.[21]

The photoswitching of charge carrier mobility was studied by standard current-voltage measurement (see Fig. 4a). The influence of charge carrier traps induced by spiropyran on charge transport was evaluated by Space Charge Limited Current (SCLC) method. The SCLC method is differential method which extracts information concerning energy distribution of traps inside the bandgap of semiconducting material from the shape of current (I) vs. voltage (V) characteristic. As the voltage applied to the sample is changed, the charge carrier concentration change in the bulk causes a shift of the Fermi level and the corresponding current. This causes the occupancy of states to change and enables to scan the distribution of energy from the current changes. The increment of the charge $\mathrm{d}n_{\mathrm{sL}}/\mathrm{d}E_{\mathrm{F}}$ due to the shift of the Fermi level E_{F} with applied voltage V can be written in the form[22,23]

$$\begin{aligned}\frac{\mathrm{d}n_{\mathrm{sL}}}{\mathrm{d}E_{\mathrm{F}}} &= \int_E h(E)\frac{\mathrm{d}f(E-E_{\mathrm{F}})}{\mathrm{d}(E-E_{\mathrm{F}})}\mathrm{d}E \\ &= \frac{1}{kT}\frac{\varepsilon\varepsilon_0 V}{eL^2} \\ &\quad\times\frac{2m-1}{m^2}\left[1+(2+3m)B+\frac{\mathrm{d}\ln(1+B)}{\mathrm{d}(\ln V)}\right]\end{aligned} \tag{4}$$

where $f(E\text{–}E_{\mathrm{F}})$ is the Fermi–Dirac statistical occupation function, E is the energy, k is the Boltzmann constant, T is the temperature, $\varepsilon\varepsilon_0$ is the electric permitivity, e is the unit charge, L is the electrode distance and $m = \mathrm{d}(\ln I)/\mathrm{d}(\ln V)$ is the slope of the experimental current-voltage ($I(V)$) characteristic. The parameter $B = [\mathrm{d}m/\mathrm{d}(\ln V)]/[$

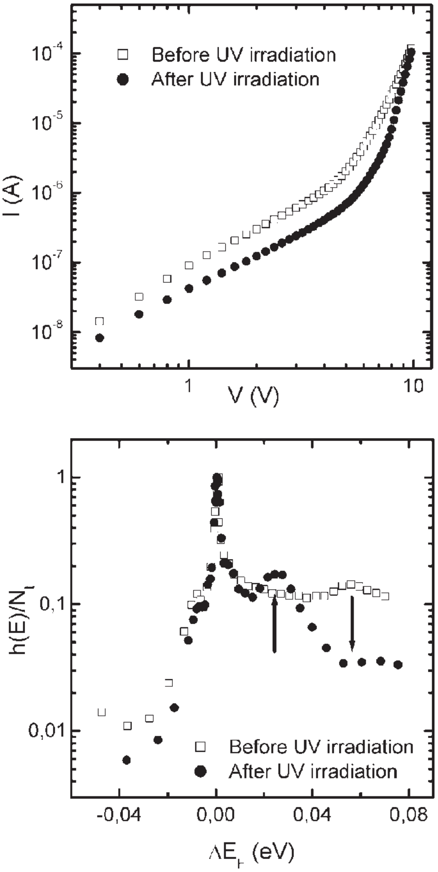

Figure 4.

Top: the current-voltage characteristics of the ITO/PEDOT/MEH-PPV:SP/Al (30% by wt.) sample before (□) and after (●) the photochromic conversion of spiropyran molecules by irradiation of UV light. Decrease in the current flowing accompanied by the change of the shape can be clearly seen. Bottom: The normalised distribution of energy states on the shift of the Fermi level centred around the common trapping level $\Delta E_F = E_F - E_t$. The arrows depict the decrease of the density of traps introduced by the spiropyran molecules and the creation of new trapping level due to the formation of metastable (photo)-merocyanine. See text for further discussion.

$m(2m-1)(m-1)]$ reflects the influence of the second derivative of the $I(V)$ on the total charge carrier concentration n_{sL}. The $h(E)$ function is called density of states (DOS) and can be obtained after the deconvolution of the integral in (4). In the case of gradual changes in the density of states one can assume that $dn_{sL}/dE_F \sim h(E)$. Since this condition is fulfilled we will use this simplification in further discussion.

Figure 4 shows the influence of the spiropyran photochromic conversion on the current flowing. The top of the figure shows the experimental $I(V)$ characteristic in the bilogarithmic scale. It can be seen that the current is decreased and also that the shape of the dependence has changed. In the first region (0–4 V) the slope of the two characteristics approaches identically to $m = 2$, suggesting that the currents are governed by the presence of one shallow trapping level with concentration N_t at the position E_t. Above this region the slope increases differently according to their respective density of energy states.

The bottom of the Figure 4 reveals the distribution of the energetic levels normalised to the maximum of the most populated trapping level $h(E)/N_t$ common to both of the systems on the shift of the Fermi level ΔE_F. It has to be noted that the thermodynamic Fermi level after the spiropyran conversion was shifted by about 0.02 eV towards the LUMO orbital. The figure uses recalculated energy axis centred on the common trapping level $\Delta E_F = E_F - E_t$, which is the most populated. It can be clearly seen that the minor trapping level situated at 0.06 eV under the reference E_t was reduced after the photochromic conversion. On the other hand new level appeared at about 0.02 eV. Since this effect is reversible, we attribute this switching to the creation of the metastable (photo)merocyanine and extinction of spiropyran molecules, respectively.

Conclusions

The new molecular photosensor based on photoswitching of charge carrier mobility was demonstrated. The quantum chemistry calculations showed that the presence of polar additive in the vicinity of polymeric chain modifies its transport levels. This increase in the energetic disorder eventuates in the decrease of the hole mobility. The change of the additive dipole moment from ca. 6 D to 12 D, which corresponds to the studied photochromic reaction, results in an almost five-fold decrease of the on-chain mobility. The experimental behaviour of the system explored by means of SCLC method showed a change of the density of states in the bandgap of the polymer. Reversible creation of new trapping level during the photochromic conversion was observed. According to the trap controlled hopping model for the description of charge transport, the presence of new trapping level results in the decrease of the charge carrier mobility as predicted by the theoretical calculations.

Furthermore, the presence of polar centres produced by photochromic conversion of the spiropyran molecules led to a quenching of the polymer photoluminescence and in the case of high concentration of SP (30% wt.) in a P(MEHPV-alt-PV), radiative energy transfer was observed. This is in agreement with our previous work,[20] where the switching was demonstrated as a drop of polymer photoconductivity.

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