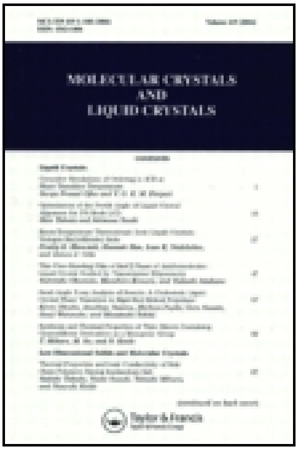

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Charge Mobilities in Molecular Materials Reversibly Modified by Light: Towards a Molecular Switch

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Charge Mobilities in Molecular Materials Reversibly Modified by Light: Towards a Molecular Switch

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Transport of charge carriers in molecular materials is influenced by traps created on or in the vicinity of polar additives. Relevant parameters of the polar dopant (dipole moments, ionization energies, electron affinities) can be reversibly changed by photochromic reactions. In conjugated polymers containing suitable photochromic species, these changes may result in opening or closing a path for a charge carrier traveling on the polymer chain.

Keywords: charge mobility; photochromism; poly[methyl(phenyl)silylene]; spiropyran; switching

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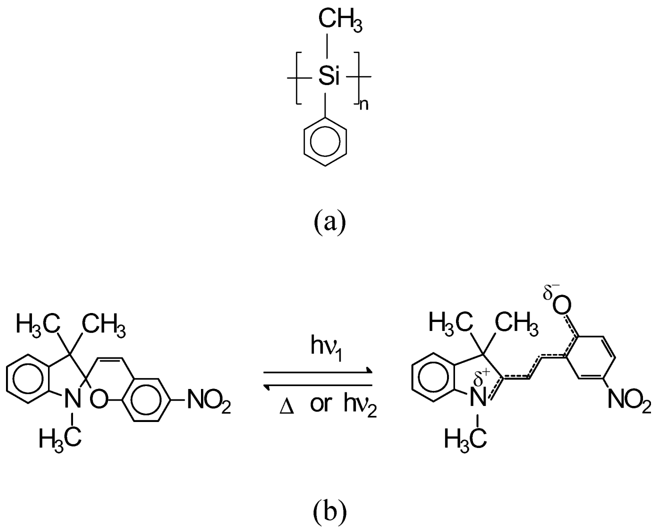
INTRODUCTION

Photochromic molecules are a good example of bistable molecular systems. Upon exposure to radiation of a specific wavelength, these systems undergo reversible photochemical reactions, reverting to their original forms when irradiated with light of a longer wavelength or stored in the dark. The process, manifesting itself in reversible changes of their absorption spectra and of several other physical parameters such as dipole moment, ionization energy etc., can be regarded as a switching between a stable and metastable state. Photochromic molecules can be coupled with charge transporting polymers to develop materials whose electrical properties would be modified in a controlled way by incident light. Such materials could be used as a kind of direct 'opto-electronic transducers', on both, micro- and macroscopic scale [1,2]. The basic principle of action of such a material would consist in a controlled modulation of the charge mobility due to the creation and annihilation of local states trapping charge carriers [3–5] and modifying the distribution of transport states [6]. Limiting oneself to the trapping of holes, one can distinguish two cases: (*i*) a molecular material is doped with guest molecules, their ionization energy being lower than that of the host ones, and (*ii*) the energy of electrostatic interactions of a charge carrier with surrounding molecules (polarization energy, P) is locally modified due to the presence of polar species. The former case is equivalent to the creation of chemical traps for holes [3], the trap depth being approximately equal to the difference of the ionization energies. In the latter case dipolar traps are created, their depth depending on the dipole moment of the guest molecule [4,5].

In this paper we present results demonstrating reversible changes of the electrical dark current and photocurrent in a molecular system composed of a photochromic system and a photoconducting polymer. The changes have been attributed to a reversible creation and annihilation of traps, the interpretation being based on the model developed in our earlier publication [7].

EXPERIMENTAL

The photoconducting polymer used in our experiments was poly[methyl(phenyl)silylene] (hereafter referred to as PMPSi – Scheme 1a), the photochromic molecule was 6-nitro-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (SP). The latter molecule undergoes a reversible photochemically driven reaction (see Scheme 1 b), resulting in production of highly polar merocyanine (MR).



SCHEME 1 Formulae of the molecules under study.

PMPSi was prepared by the Wurtz coupling reaction [8]. Photochromic SP was purchased from Aldrich and used without further purification. The concentration of SP in SP/PMPSi samples was 5 mol %. Thin films used in electrical measurements were prepared from a toluene solution by casting on conducting ITO glasses. The current was measured using a Keithley 6517 A electrometer.

RESULTS AND DISCUSSION

Figure 1 shows a family of dark current-voltage (*j–U*) characteristics measured on a 600 nm thick sandwich sample ITO/PMPSi-SP/Al. The curve measured on the pristine sample (curve 1) was ohmic up to 2 V turning to a superlinear dependence at higher voltages. After the sample was illuminated with a 340 nm radiation resulting in the formation of the polar MR form, the current decreased by ca. one order of magnitude (curve 2). The change was reversible, the current increasing asymptotically to the values measured before the illumination.

Results of measurements of the rise and decay of the photocurrent, carried out on surface samples PMPSi + SP|Al-Al, are shown in Figure 2. After the illumination of the sample with a low intensity 340 nm radiation, a photocurrent was observed, increasing to its steady state value attained after a few minutes (curve 1). The kinetics of the photocurrent generated with a more intense UV light used for the photochromic SP → MR transformation was quite different (curve

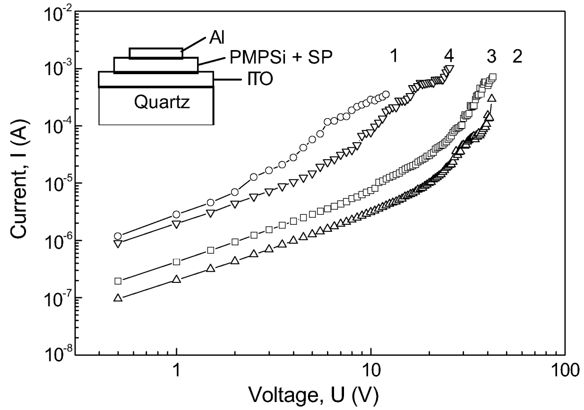


FIGURE 1 Dark current-voltage characteristics of an ITO/PMPSi-SP/Al sandwich sample before and after UV illumination. Curve 1 – pristine sample, curve 2 – measured immediately after UV illumination, curves 3 and 4 – measured after 3 hrs and 24 hrs, respectively, relaxation in vacuum, at room temperature. Inset: Experimental arrangement.

2): after an abrupt initial rise, the photocurrent decreased with time. A repeated experiment performed on the same sample after formation of the coloured MR species, is shown on the right side of Figure 2: the "low intensity" photocurrent (curve 1′) was ca. 6 times lower than the photocurrent measured before irradiation in the same conditions (curve 1).

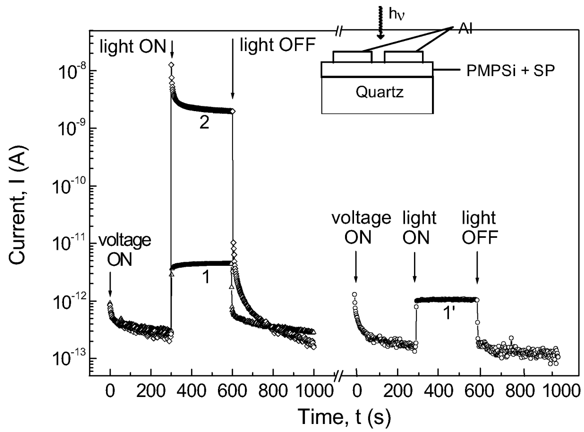


FIGURE 2 Photocurrent kinetics measured on a surface-type sample PMPSi-SP/Al-Al, in vacuum. Inset: Experimental arrangement.

Both experiments can be interpreted assuming the kinetics of the process being governed by two competing kinetic processes driven by light: reversible formation of traps (whether dipolar or chemical) due to the photochromic SP→ MR reaction, and a trapping/detrapping of charge carriers in the traps formed in such a way. The situation is well described by a semi-quantitative model developed in our paper [7].

TOWARDS A MOLECULAR SWITCH

The reversible changes of electrical properties of macroscopic samples reported in the preceding section can be understood as resulting from changes of properties of individual molecules. One may thus envisage a molecular scale device based on changes of the on-chain mobility of charge carriers due to a photochromic reaction. Such a system ("molecular switch") has been designed based on quantum chemical calculations reported in detail elsewhere [9]. The system consists of a molecular wire (here PMPSi) with a photochromic side group (here SP) chemically attached to the polymer by a spacer (here

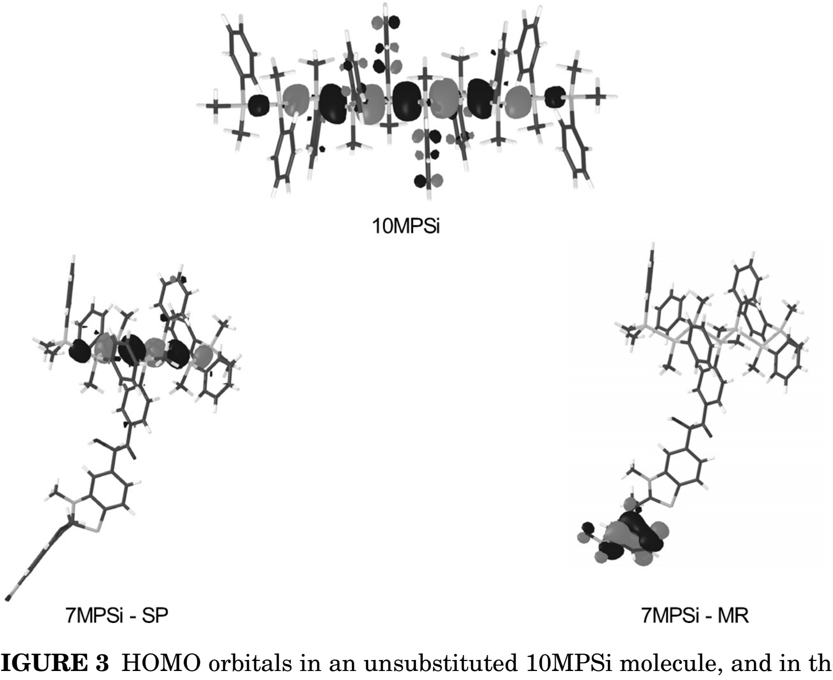


FIGURE 3 HOMO orbitals in an unsubstituted 10MPSi molecule, and in the 7MPSi-SP and 7MPSi-MR systems.

−C(O)−C(H)OH−). As follows from the quantum chemical calculations [9], the dipole moment of the separate stable (SP) moiety amounts to ca. 5–6 D depending on the substituents, whereas the moment of the metastable form (MR) exceeds 12 D. Thus one may estimate that a suitably oriented dipole placed in the position of the stable form would create on the chain a dipolar trap ca. 0.10 eV deep, whereas the metastable form placed in the same position would create a dipolar trap ca. 0.24 eV deep.

Independently, the effect of the chemical trapping should be considered. If the spacer allows for the electronic coupling of the side group and the polymer chain, an excess carrier may be localized on the side group provided the energetic conditions are fulfilled. A chemical hole trap will be created if HOMO is localized on the side group. Our calculations performed on oligomers of PMPSi (dekamer and heptamer – cf. Fig. 3) demonstrate that the side group in its stable form group would not act as a chemical trap for holes. Upon switching, however, a chemical trap would be formed, its depth amounting to ca. 0.3–0.5 eV, depending on the effective conjugation length of the Si-Si σ bonds of the chain.

CONCLUSION

The reported results demonstrate that it is possible to prepare a system consisting of charge transporting polymer containing photochromic species whose electrical properties would be modified by a reversible photochemical reaction resulting in the creation and annihilation of traps. Creation of two types of traps is possible: dipolar traps, where a carrier traveling on the polymer chain is localized due to electrostatic interactions with dipoles of a variable polarity, and/or chemical traps resulting from local changes of the HOMO energy. It is expected that materials consisting of electroactive matrices functionalized with suitably chosen photochromic species (admixed molecules or chemically attached side groups) may be used as elements of electro-optical systems or bistable switches.

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