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Photochromic Systems as Models for Opto-Electrical Switches

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A short overview of research into design of molecular opto-electrical switches is presented. Theoretical results obtained on microscopic systems are supplemented with experimental results measured on macroscopic structures fabricated using molecular materials. It is shown that, beside optical switching of the type: "optical input" – "optical output", photochemically driven photochromic reaction may be, under certain conditions, used as a controlling step in "optical input – electrical output" devices. Several possible architectures of such systems are described.

Keywords Charge carrier transport; molecular material; opto-electrical switch; photochromism

1. Introduction

The most important trends in electronics and photonics observed in recent decades have been miniaturization of the elements of devices, and widening of the spectrum of materials used in these devices. Among novel materials, low-molecular weight organic and organometallic compounds as well as polymers have been successfully commercialized during last two decades, paving the way to organic electronics (see, e.g., [1–6]). For the matter of this paper, it is important to note that the most characteristic property of this class of materials, generally falling into the category of molecular materials [7–9], is a large difference between the energy of intra- and intermolecular interactions: the former one is of the order of 10^2–10^3 kJ/mol, whereas the latter is typically one order of magnitude lower. Consequently, many properties of molecular materials (understood as macroscopic assemblies of molecules) can be directly related to the properties of individual molecules. This is an important property of molecular materials: theoretical predictions based on calculations performed on individual molecules can (at least, in principle) be verified with

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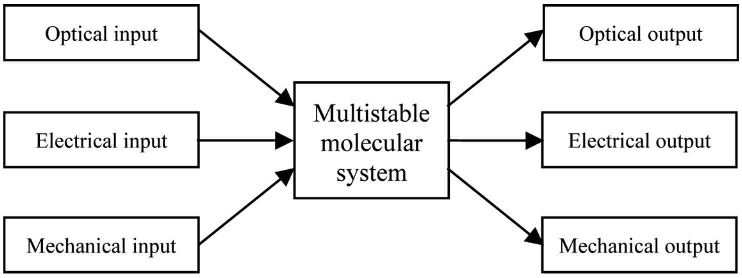


Figure 1. A schematic diagram of a molecular switch employing optical, electrical or mechanical stimuli, and optical, electrical or mechanical detection.

experiments carried out on samples consisting of mezo- and macroscopic assemblies of molecules, irrespective of dimensions of the samples.

The miniaturization of electronic elements has been adequately described by the heuristic Moore's law [10], according to which the density of packing of electronic elements increases exponentially, i.e., the size of an average element of an electronic circuit decreases exponentially with time. The trend has been fulfilled for half a century; rough estimations indicate that the size of an element should approach nanometric (i.e., molecular) dimensions around the year 2020.

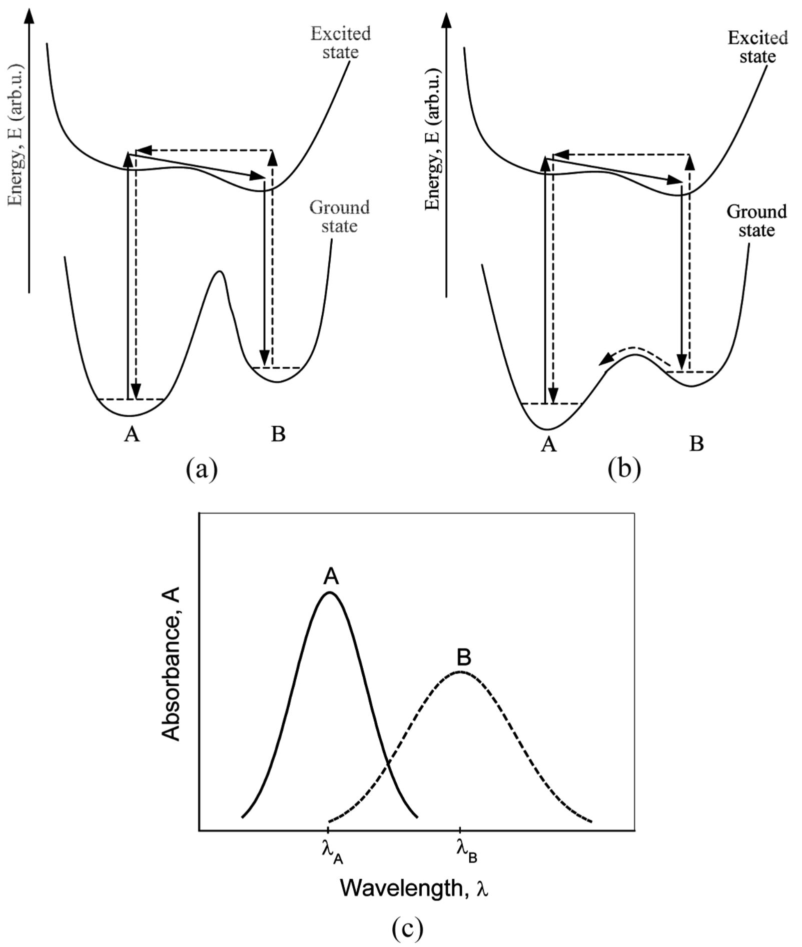
Thus, a natural question arises whether suitably functionalized molecules can be employed as elements of nano-scale electronic/photonic systems. There have been numerous reports on successful attempts of fabricating molecular wires (see, e.g., [11,12]) and molecular rectifiers (e.g., [13–19]); at the present stage, however, the principal difficulties have been encountered in attaching molecular devices to an external world and addressing them. On the other hand, these nano-systems can serve as models for macro-scale organic electronic devices.

This paper presents a short overview of results concerning the construction of molecular switch. Theoretical results obtained on microscopic systems will be supplemented with experimental results measured on macroscopic structures fabricated using organic low-molecular weight and polymeric materials.

According to a general definition, a switch is a mechanical, electrical, electronic, or optical device for opening or closing a circuit, or for diverting energy or charge from one part of a circuit to another. In its "textbook" version, switches can be driven by electrical, optical, or mechanical stimuli; the resulting changes can be detected as modulation of electrical, optical or mechanical parameters of the system (Fig. 1).

2. Photochromism and Photochromic Materials

It follows from the above definition that an inherent part of a switch is a multistable element differing in properties in each of its states. Such systems are quite frequent in the world of molecular materials: if one limits oneself to optically driven systems ('optical input'), then photochromic materials come as a natural choice. The photochromic process is a reversible reaction, in which elementary reaction in at least one direction is driven by light. The reverse reaction may be either driven by light of different quantum energy or thermally activated (Fig. 2). The reactant and product, being two different species, usually differ in their electron absorption spectra and their electronic systems get excited at different wavelengths. In other words,



(a) (b)

(c)

Figure 2. Schematic energy diagrams of the photochromic switching process between a reactant **A** and product **B**. The **A**→**B** reaction is realized by optical stimulation via the excited electronic state. (a) The reverse reaction is possible only via the excited state because of high ground state barrier between **B** and **A**. (b) Due to a low ground state energy barrier, the reverse reaction may occur both photochemically (the same reaction path as in (a)) and thermally. (c) Absorption spectra associated with the transitions between electronic levels of the **A** and **B** molecules.

excitation of the reactant **A** results in the photochemical reaction producing the product **B**, whereas excitation of **B** results in production of **A**. Simplified schemes of energy levels of two types of photochromic systems and schematic spectra of the two forms are shown in Figure 2.

In molecular photochromic systems, the energies of the ground states of both forms are different. Thus, strictly speaking, only one form (reactant) is *thermodynamically* stable. For a proper action of the system, however, it is sufficient that the other form be *kinetically* stable, i.e., the observation time of the experiment is sufficiently shorter than the inverse of the rate constant of the reverse reaction. The kinetics of the reverse reaction depends on the height of the barrier between the ground state and the transition state: for the barrier exceeding ca. 15–20 kT (Fig. 2a), only photochemically driven reverse reaction is possible (this class of photochromic systems is sometimes referred to as P-systems), otherwise thermally activated reaction may occur (T-systems, Fig. 2b), its rate depending on the barrier height.

It is beyond the scope of this paper to describe in detail chemistry of photochromic families; the reader is referred to numerous monographs and collections of papers [20–24]. It will be useful, however, to present photochromic families whose properties will be discussed in the subsequent parts of this paper.

Azobenzene and Its Derivatives

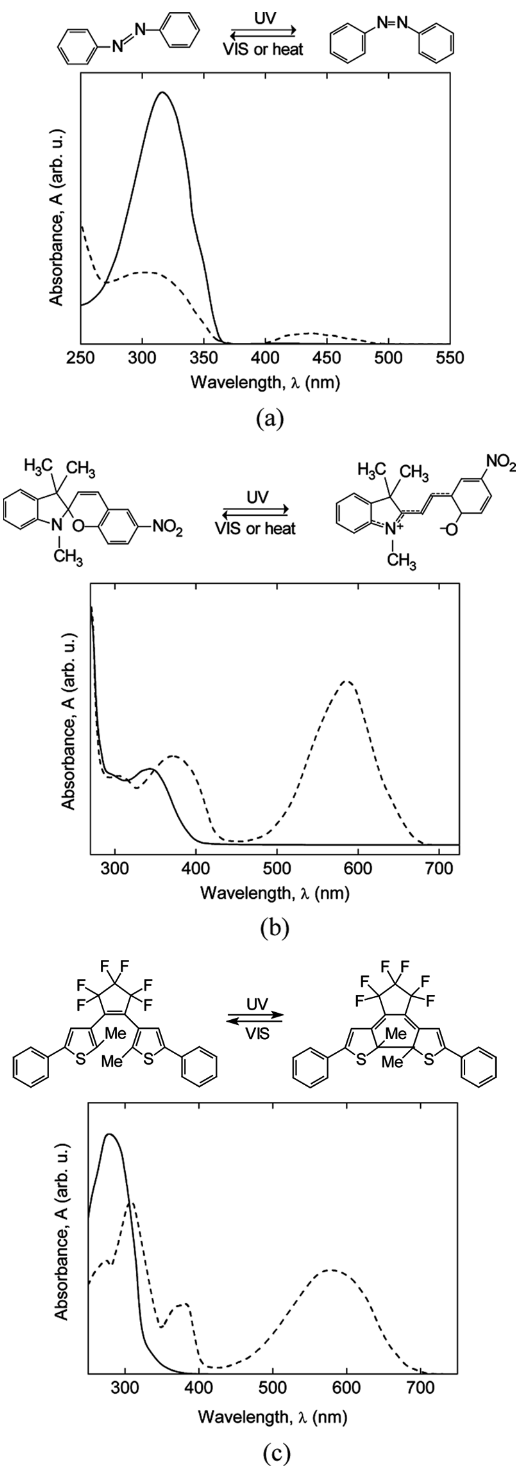
Azobenzenes have been the most extensively studied family of photochromic compounds. The compound exists in two forms: thermodynamically stable *trans* (*E*) form and metastable *cis* (*Z*) form, the photochromic cycle being a reversible isomerization. The molecular formula of parent (unsubstituted) azobenzene, the reaction scheme, and the UV-Vis spectra of the two forms are presented in Figure 3a. The forward (*trans*-*cis*) reaction is photochemically driven by illumination into the absorption band of the *trans* form (ca. 320–350 nm), whereas the reverse process is usually thermally activated or driven by illumination into the n-π^* band (ca. 450 nm). The molecule can be modified by substitution with various functional groups or by incorporation into a larger molecular aggregate (e.g., a polymer chain); the modifications may change properties of the system (e.g., spectra and reaction kinetics).

Spiropyrans

The characteristic feature of this photochromic family is the presence of spiro-carbon: one can state, with some degree of simplification, that the molecules consist of two moieties, their planes being nearly perpendicular to one another. The reaction consists in a heterolytic bond cleavage and ring opening. The spectra of both forms of the system depend on substituents but the stable (closed) form usually does not absorb in the visible, whereas the metastable form, similar to the merocyanine dye, exhibits a strong absorption in this spectral region. It should be noted that the formation of the metastable form requires a substantial reorganization of the geometry of the molecule. The molecular formula of a representative spiropyran, the reaction scheme, and the UV-Vis spectra of the two forms are presented in Figure 3b.

Diarylethenes

The formulae of the stable and metastable form of an exemplary diarylethene, together with the reaction scheme and spectra of the two forms, are shown in Figure 3c. In its stable form, the molecule consists of two homo- or heteroaromatic moieties, linked with the double –C=C– bond. Usually, the carbons are additionally connected with a rigid link, and the aromatic rings contain a bulky group causing an overcrowding. As a result, the open form is thermodynamically stable; the irradiation leads to closing the –C–C– bond between the adjacent positions in the two rings. Due to presence of the additional link, the molecular volumes of both forms do not differ much, and the reaction does not require much space.



(a)

(b)

(c)

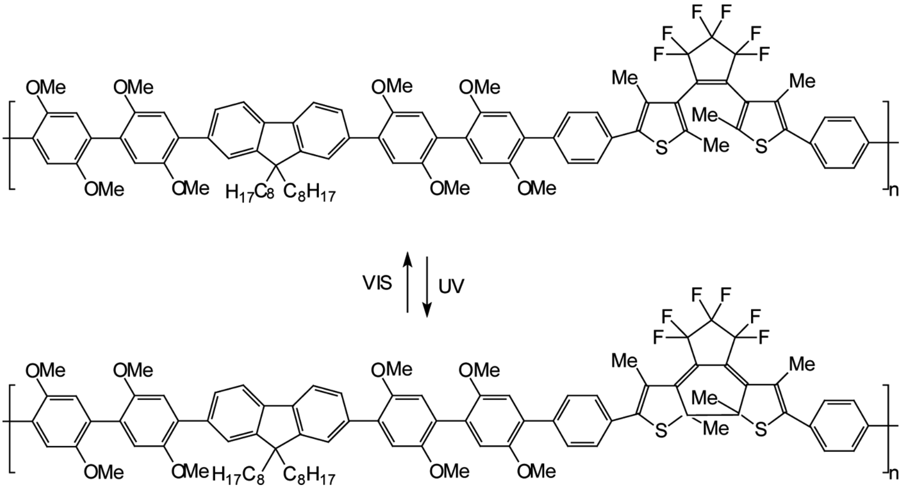
Figure 3. Photochromic reactions and spectra of representatives of three photochromic families: (a) azobenzene; (b) spiropyran; (c) diarylethene. The full lines represent spectra of stable forms of the systems, dashed lines are spectra of metastable forms.

3. Opto-Electrical Switches Based on the Photochromic Effect – Principles

It appears from the discussion in the preceding section that any photochromic system may be considered as a switch of the "optical input – optical output" type: excitation of the reactant with a wavelength from its absorption band results in a change of absorbance in the absorption band of the product, whereas excitation of the product with a wavelength from its absorption band results in a change of absorbance in the absorption band of the reactant. For many purposes, however, it would be more convenient to record directly an electrical response of the system (one must bear in mind that the electric signals may easily undergo amplification and long distance transmission). In other words, it would be desirable to construct a switch of the "optical input – electrical output" type. In such a switch, an optical excitation would result in a change in the concentration and/or the mobility of charge carriers.

Conceptually, the simplest way to achieve the desired effect is to incorporate a suitable photochromic molecule into the chain of a conjugated polymer. This approach has been employed by Kawai *et al.* [25] who incorporated diarylethene into a poly(phenylene-fluorene) chain (Scheme 1). In its stable form, diarylethene lacks conjugation between the two moieties, thus electrically, the system is in the "off" state. Upon excitation with UV radiation, the conjugation path is opened and the system is switched to the "on" state. The irradiation with the visible light, stimulating the reverse reaction, switches the system back to the "off" state.

Another concept was put forward by Nešpůrek, Sworakowski *et al.* [26–31]. According to their model, the system consists of a matrix formed by network of conjugated polymer chains or a network of molecules enabling the transport of carriers ("molecular wire") and a switchable photochromic molecule, either chemically attached to the wire (Fig. 4) or dispersed in the material. The mobility of charge carriers is controlled by traps, created and annihilated in a controlled way by the photochromic reaction. In the forthcoming discussion, we will limit ourselves to the hole trapping, most often encountered in typical molecular solids.



Scheme 1. Chemical structure of the polymer used for measurements of the influence of chain conjugation on switching ability [25].

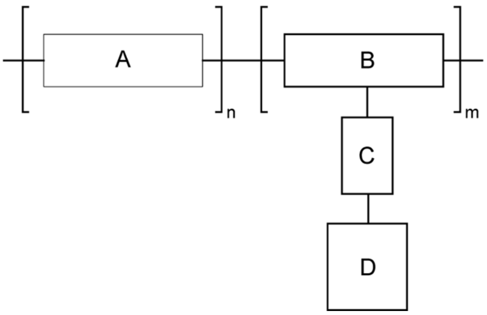


Figure 4. Architecture of a molecular switch based on charge transporting copolymer (segments A and B) and photochromic active group D, chemically attached via the spacer C [26].

Two types of traps can play role in the process: chemical traps and dipolar traps. The former ones may be formed by the dopant molecules, their depths depending on the difference of ionization energies of the matrix (I_h^g) and the dopant (I_d^g). To a first approximation, neglecting secondary effects, one may write [32]

$$E_t^{chem} \approx I_h^g - I_d^g \tag{1}$$

where the superscript g indicates the ionization energy of an isolated molecule. According to the convention adopted throughout the paper, trap depths will be positive.

The dipolar traps [33–37] are formed on molecules adjacent to the dopant if the dopant molecule is polar (i.e., possesses a non-zero permanent dipole moment), and the matrix is either non-polar or weakly polar. In this case, the trap depth is approximately equal to the interaction energy of the dipolar dopant and the carrier situated on an adjacent molecule (molecular segment) of the matrix. In the simplest case of non-polar isotropic matrix and the most favourable orientation of the dipole, the approximate expression reads

$$E_t^{dip} \approx \frac{ep}{4\pi\varepsilon\varepsilon_o r^2} \tag{2}$$

where e is the unit charge, p stands for the permanent dipole moment of the dopant, ε is the relative electric permittivity of the matrix, ε_o – permittivity of free space, and r is the distance between the charge and the dipole. The trap depth is thus proportional to the dipole moment of the dopant. More exact calculations performed on a model molecular lattice showed that traps as deep as 0.7 eV can be created in the vicinity of a dipole whose permanent moment amounts to 12 D, on a molecule 0.6 nm apart (see Fig. 5).

A more realistic case would be a photoconducting polymer matrix, with a dipole attached to the polymer chain with a spacer [30]. Let us estimate the depths of traps formed in a molecular switch consisting of spiropyran shown in Figure 3b, attached to the poly[methyl(phenyl)]silylene chain (PMPSi) (Scheme 2). Quantum-chemical calculations performed on the HF/3-21G$^{(*)}$ level for the stable and metastable forms of the photochromic system (SP and MR, respectively) yielded the results listed in Table 1.

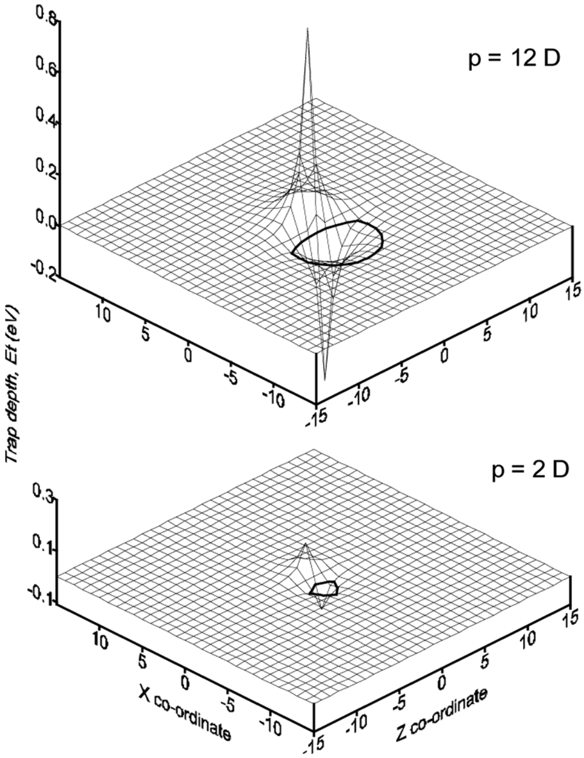
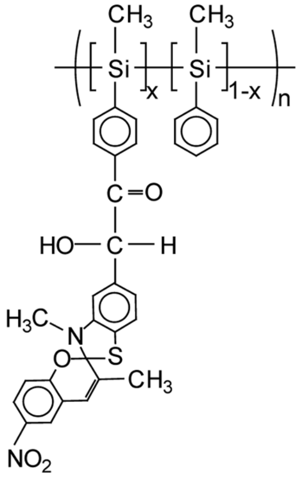


Figure 5. Trap depths for holes created in a regular lattice in the vicinity of polar centres of two polarities (2D and 12D). The dipoles are located at the origins, their positive poles pointing in the positive directions of the y axes. The nodes of the grids represent molecules, the figures showing two-dimensional cross-sections through three-dimensional lattices taken at z = 0 (trap depth axis) [37].



Scheme 2. Synthetic realization of the architecture shown in Figure 4: poly[methyl(phenyl) silylene] copolymer containing spiropyran (1′,3′,3′-trimethyl-6-nitrospiro[2H-1-chromene-2,2′-indoline]) side group, linked through the –C(O)–C(HOH)– spacer.

Table 1. Estimated depths of chemical and dipolar traps formed in the system shown in Scheme 2. The results of quantum-chemical calculations taken from [30]

	I^g (eV)*	p (D)*	r (nm)*	E_t^{dip} (eV)#	E_t^{chem} (eV)
PMPSi	7.2				
SP	8.0	8.1	1.3	0.05	<0 (no trap)
MR	6.8	18.5	1.3	0.11	0.3

*Data taken from [30].
#Calculated from Eq. (2) assuming $\varepsilon = 3$.

It follows from the above estimates that the effect should indeed exist but the traps formed are too shallow to yield an observable effect at ambient temperature. Thus one should optimize the system: (i) the present system may be operative at lower temperatures; (ii) the spacer should be shortened in order to increase the charge-dipole interaction energy; (iii) finally, one should look for a system allowing for formation of deeper traps (it seems that the diarylethene system in an appropriate polymer matrix might serve as a better model). The opto-electrical switching may also be achieved employing other effects as will be discussed in the next section.

4. Opto-Electrical Switches Based on the Photochromic Effect – Experiment

"Optical input – electrical output" switches can be made on molecular scale, for example, using a diarylethene derivative molecule. Early measurements showed that the photoswitching from the closed ring to the open ring form decreased the conductivity by three orders of magnitude; the effect, however, could be observed only once [38]. The irreversibility was explained by the vicinity of the gold wire to the diarylethene ring. Reversible photoswitching with the on-off ratio equal to 2.5 was achieved using phenyl spacer separating the diarylethene molecule from gold electrode [39]. It is noteworthy that a macro-scale molecular switch made of a diarylethene derivative dispersed in polystyrene exhibited the on-off ratio amounting to 2.9 [40].

The photoswitching of diarylethene molecule has been very sensitive to substituents, electrodes and anchoring configuration [41]. For example, taking into account possible differences in the experimental arrangement, one may note that the on-off ratio of conductivity switching was better for diarylethene molecule attached to carbon nanotube electrodes as compared with a similar material supplied with gold electrodes. The experimental on-off ratio of currents between open and closed isomers attached to the nanotubes was reported to amount to 25 [42]. It should be mentioned, though, that the quantum-chemical calculations predicted the on-off ratio over 2 orders of magnitude [41,43].

It follows from the above examples that experimental realization of an opto-electrical switch on a nano-scale structure has been achieved in very few cases. It was, however, mentioned in Section 1 that, due to weak intermolecular interactions in typical molecular systems, molecules retain their individuality in mezo- and macroscopic assemblies; thus many properties of such assemblies may be deduced directly from respective properties of individual molecules. Consequently, one may expect, for example, that the switching would be observed in macroscopic samples of the polymer shown in Scheme 1. This has indeed been the case: Kawai *et al.* [25] observed the switching in the system consisting of a thin film (ca. 100 nm) of the polymer spin-coated onto an ITO covered quartz substrate, the top electrode being vacuum-evaporated Au. The results are shown in Figure 6: the switching ratio depends on temperature, the room temperature value not exceeding 2.

The opto-electrical switching may also be achieved utilizing changes of properties of macroscopic assemblies of photochromic species – either pure, used as elements of the structure (e.g., in the form of thin films) or dispersed in matrices. A model, assuming the action of the switch being controlled by injection of carriers, i.e., by properties of the interface between the metallic contact and the active layer was put forward by Jakobsson *et al.* [44]. The authors performed calculations according to the Arkhipov model [45,46] for injection currents across metal-organic and organic-organic interfaces providing guidelines for construction of efficient opto-electrical switch. The modelling allowed to choose an organic semiconductor – photochromic material – metal multi-layer system that could significantly modulate the current under phototransformation of photochromic molecules. The important parameter is the relation between the ionization energies of both forms of the photochromic system and the work function of the electrode. In some materials, the ionization energies (HOMO energies) of both components of the photochromic pair are quite different (as, for example, is the case of diarylethene). The change of ionization energy alters the energy difference between HOMO of the photochromic material and Fermi level of an electrode, resulting in a change of the injection barrier for holes and hence the current through the structure [44]. The on-off ratio of current is predicted to be over three orders of magnitude when the injection barrier changes from 0.3 to 0.5 eV. Considering injection of holes, the highest on-off ratio is expected when HOMO of the open form of the photochromic system is lower than HOMO of organic semiconductor, while HOMO of the closed state is between Fermi level of metal and HOMO of semiconductor. The latter condition replaces a high injection

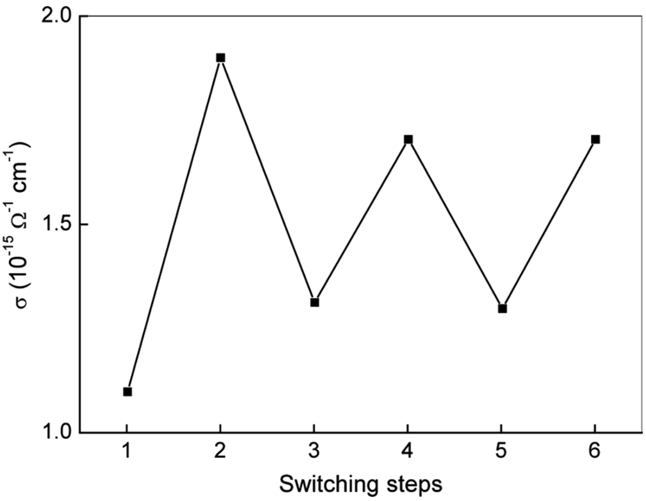


Figure 6. The switching steps in electrical conductivity of sandwich structure ITO||conjugated polymer with incorporated diarylethene units (Scheme 1)||Au (data taken from [25]).

barrier by two lower ones allowing a more efficient charge carrier transport through the multi-layer structure [44]. In the same way a shift of LUMOs may change injection of electrons in n-type materials.

Two kinds of thin film photochromic switches were proposed by Honma and Yokoyama employing change of hole injection from a metal electrode to an organic layer [47]. One of the structures consisted of a thin film of a photochromic material between hole transporting organic layer and metal electrode (Fig. 7), and the other one was a sandwich cell consisting of a photochromic material dissolved in a polymeric matrix between two electrodes. A diarylethene derivative with a large difference between ionization energies of the two forms was used: the ionization energy of the open form isomer (6.80 eV) was much higher than that of the closed form isomer (5.82 eV) due to the difference in π-conjugation. A Pt electrode with work function of 5.43 eV was used as a positive contact and low conductive polystyrene was used as a matrix. Due to a small energy difference between the ionization energy of the closed ring isomer and the work function of Pt, an efficient hole injection and, consequently, charge carrier transport were observed, while upon photoisomerisation and ring opening, the height of the interface barrier increased, preventing hole injection. The photochromic material in open ring state acted as a charge carrier blocking layer.

One should also bear in mind that in the system shown in Figure 7b the photochromic reaction (and hence an efficient switching) may be achieved if certain relations between energy levels of the matrix and the photochromic system are fulfilled:

(i) in order to prevent simultaneous excitation of the matrix and the photochromic molecules, their excitation energies should be separated ($\lambda_{PC} > \lambda_{\mathrm{matrix}}$);
(ii) in order to prevent energy transfer from the excited state of the photochromic molecules to the matrix, the energy of the excited state of the matrix (measured with respect to a common external reference) should be higher that that of the photochrom

$$\left(I_{PC} - \frac{hc}{\lambda_{PC}} > I_{\mathrm{matrix}} - \frac{hc}{\lambda_{\mathrm{matrix}}} \right)$$

(iii) The latter condition is not met in the SP/MR system dissolved in the polythiophene matrix. Thus, the photochromic reaction does not occur [48].

The structure with photochromic material between hole transporting material and electrode (Fig. 7a) was used by Tsujioka for development of a photochromic switch, in which the output was photocurrent signal [49]. The hole transporting layer was made of phthalocyanine, photoconductive under near-infrared illumination. Changes of the ionization energy of a diarylethene derivative due to the reversible photochromic reaction allowed one to control the injection of holes. The photochromic reaction was driven by UV and visible light, separated spectrally from the read-out near-infrared radiation. This structure was highly fatigue resistant switching nondestructively over 10^6 times [49]. Yassar *et al.* [50] studied novel photochromic oligothiophenes capable of switching the conductivity by two orders of magnitude and photoconductivity with an on-off ratio of 10^8. The advantage of this system is high conductivity of the photochromic isomer allowing one not to use conductive matrix in electronic device like the one depicted in Figure 7a. The photochromic

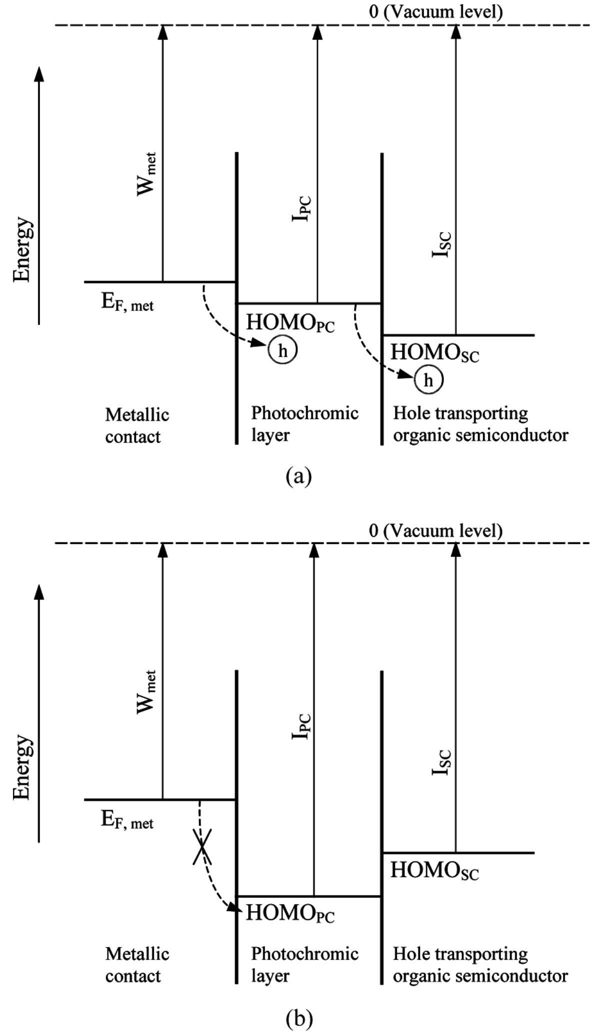
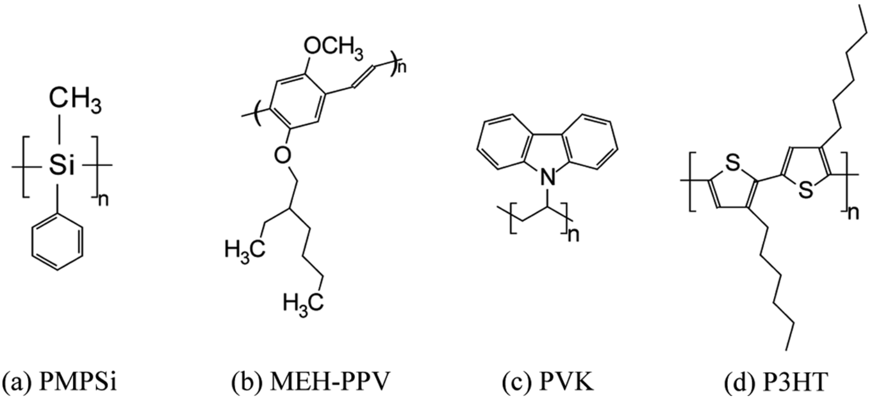


Figure 7. Energy diagrams for hole injection from a metal contact into a hole transporting organic semiconductor through photochromic layer (here, diarylethene). (a) Due to a small energy difference between the ionization energy I_{PC} of the closed ring isomer of diarylethene derivative and the work function of contact metal W_{met} the hole injection is possible and charge carrier transport takes place. (b) Upon photoisomerization and ring opening, the height of the interface barrier increases, preventing hole injection. $E_{F,met}$ is the Fermi level of the metal, I_{SC} is the ionisation energy of the hole transporting organic semiconductor (after [46]).

molecules used in [50] at ambient temperature reverse back from metastable state to its initial one overnight.

Measurements of dark currents and photocurrents in the system consisting of photoconducting polymer with a dissolved photochromic system have been reported by Nešpůrek, Sworakowski *et al.* In early reports [51–53], poly[methyl(phenyl)]silylene (PMPSi – see Scheme 3a) was chosen as the polymer matrix, whereas spiropyran (SP – see Fig. 3b) – photomerocyanine (MR) photochromic system, exhibiting a



Scheme 3. Chemical formulae of the polymers discussed in the text: (a) poly[methyl(phenyl)] silylene, (b) poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene], (c) poly(*N*-vinylcarbazole), (d) poly(3-hexylthiophene).

large difference between the dipole moments and ionization energies of the two components, was chosen as the active part of the switch. Measurements of dark current-voltage characteristics performed on sandwich sample between ITO and gold electrodes showed a decrease of the conductivity upon irradiation with UV light. The decrease amounted to ca. one order of magnitude; the system was found to return to its initial state overnight at ambient temperature (see Fig. 8). The decrease was attributed to the creation of dipolar and/or chemical traps in the vicinity of highly polar MR molecules produced during the irradiation; whereas the slow thermal recovery – to the thermal reverse reaction. Surface photocurrents, measured on the same material (PMPSi + SP/MR) revealed the existence of two kinetic effects: a rapid one, attributed to electric relaxation, and a slow one due to creation of

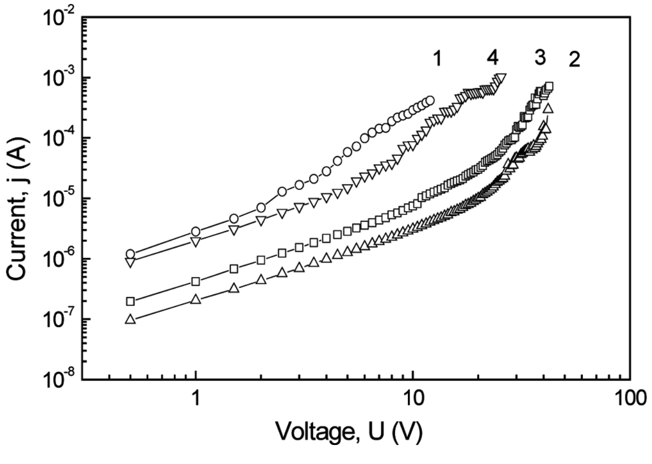


Figure 8. Dark current-voltage characteristics of an ITO/PMPSi-SP/Al sandwich sample before and after UV illumination. Curve 1 – pristine sample, curve 2 – measured immediately after UV illumination, curves 3 and 4 – measured after 3 hrs and 24 hrs, respectively, relaxation in vacuum, at room temperature.

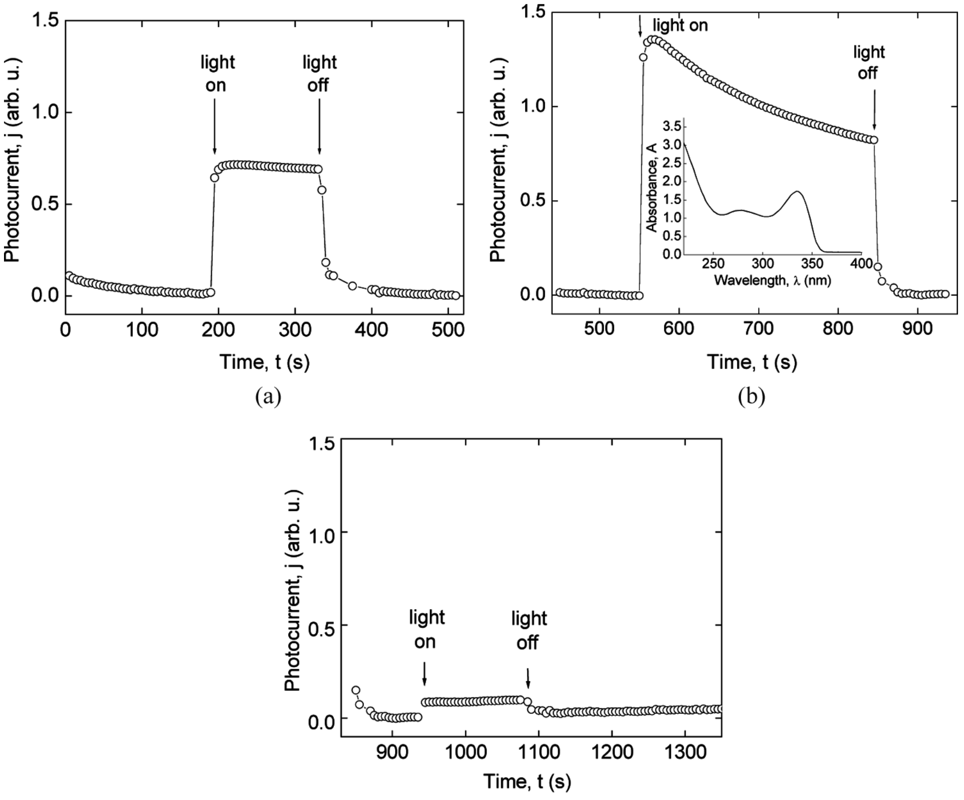
dipolar/chemical traps during UV illumination. In both cases, the results have been interpreted as due to the reversible creation/annihilation of dipolar and/or chemical traps associated with the reversible SP – MR reaction. However, taking into consideration results of the quantum-chemical calculations reported in Section 3, one should not exclude another mechanism, like the changes of the interface barrier height, already discussed in this section and silicon metastable states. Replacing PMPSi with poly(2-methoxy-5-(2′-ethylhexoxy)-*p*-phenylene vinylene) (MEH-PPV, see Scheme 3b) resulted in a decrease of the switching ratio from ca. 10 to 2 [54].

Formation of chemical traps due to photochromic reaction has been confirmed experimentally. Molecules of SP and MR have high ionization energies and are unlikely to form chemical traps for holes in photoconductive polythiophenes and MEH-PPV, but for poly(vinyl carbazole) with the ionization energy amounting to 7.6 eV, formation of shallow chemical traps is possible [55]. These results were supported by achieving the on-off ratio about 2 orders of magnitude for poly(*N*-vinylcarbazole) (PVK, see Scheme 3c) with 2.5% of SP [55].

Anderson *et al.* [55,56] measured current-voltage characteristics on sandwich structures made of MEH-PPV and poly(3-hexylthiophene) (P3HT – Scheme 3d) polymers and photochromic spirooxazine derivative. Their results seem to speak in favour of the current being controlled by formation and annihilation of traps during the photochromic cycle. The best results of photoswitching were accomplished for 20 wt% mixture of spirooxazine with MEH-PPV. Photoswitching on-off ratio of about 50 was achieved at biased voltage in the range of (5–10) V [56]. The on-off ratio for p3HT devices was much lower than that for devices based on MEH-PPV [57].

Photochromic systems with switchable dipoles have been employed as elements of field effect transistors [58–60]. The photochromic material was deposited on the surface or interface of an organic semiconductor affecting a current through transistor channel. Shen *et al.* [58] deposited SP molecules on surfaces of pentacene (p-type material) and fluorinated copper phthalocyanine (n-type material) in field effect transistors using the stamp technique. In pentacene transistors, an increase of source-drain current after UV illumination and a decrease of the current after illumination with visible light was observed, whereas an opposite effect was detected in phthalocyanine transistors: the current decreased after UV illumination and rose after exposure to visible light. The effect has been explained assuming a contribution of a local (negative) gate voltage produced by the dipoles created upon irradiation, leading to an increase of electrical conductivity in p-type field effect transistors and to a decrease of the current in n-type devices. SP added to single-walled carbon nanotube transistors also showed the photoswitching effect [59]: the source-drain current dropped after UV illumination. The effect has been explained by creation of dipole traps for charge carriers by highly polar photomerocyanine (MR) molecules produced by the photochromic reaction.

A ‘FET-like photoactive device’ has been described by Kratochvílová *et al.* [60]. The device consisted of photoconductive film of metal-free phthalocyanine deposited on a thin film of PMPSi with dissolved SP. Illumination of the structure with the visible light ($\lambda = 625$ nm – neither PMPSi nor SP absorb in this spectral region) resulted in an increase of the current due to photoconductivity of phthalocyanine; the current reached a steady state within seconds, decaying rapidly to its initial value after the illumination has been switched off. Illumination of the sample with UV ($\lambda = 350$ nm) absorbed by SP resulted in a rapid increase of the current due to the photoconductivity, followed by a slow decrease. A subsequent illumination with the $\lambda = 625$ nm



(a) (b)

(c)

Figure 9. Photocurrent kinetics in photo-FET devices: (a) Sample illuminated with the visible light ($\lambda = 625\,\text{nm}$); (b) Sample illuminated with UV ($\lambda = 350\,\text{nm}$); (c) Sample illuminated with the visible light ($\lambda = 625\,\text{nm}$), after the exposure of the sample to UV. Inset in (b): Absorption spectrum of PMPSi [60].

light gave rise to an increase of the current, its magnitude, however, being much lower than that in the first cycle. The slow decrease of the current during the second cycle, and its much lower magnitude during the third cycle were rationalized assuming the current in the phthalocyanine layer being affected by the field of dipoles produced in the polymer film during the photochromic reaction. The field from the dipoles produced in such a way acted as an equivalent of the gate field in FET devices. The experimental result is shown in Figure 9.

5. Final Remarks

The opto-electrical switch – a device where an optical excitation would result in a change in the concentration and/or the mobility of charge carriers – seems to be an advantageous electronic element. In some cases, it is convenient to record an electrical response because electric signals may easily undergo amplification during long distance transmissions. For high frequency applications both parts of the switch, optical and electrical, must be quite fast. The optical "excitation" part would be realized by photochromic materials which themselves represent switches of the "optical input – optical output" type. The photochemically driven reaction must fulfil several conditions: (i) good chemical stability even in short wavelength part of the spectrum (it would be better to realize the excitation by visible light with lower photon energy); (ii) fast photochemical reaction with small conformational changes of photochromic molecules – the large change of molecule morphology makes the photochromic reaction slow; (iii) in the case of composite consisting of a polymer and photochromic additive, the polymer must have high free volume. Moreover, certain energetic conditions have to be met: (iv) In order to prevent uncontrolled thermal reverse reaction, the ground state energy barrier between both forms of the photochromic system must be sufficiently high, (v) the difference of dipole moments and/or ionization energies of both forms should be as large as possible, (vi) absorption of the photochromic system should be separated in energy from that of the matrix, (vii) the energies of the excited states of the photochromic system and the matrix should prevent the energy transfer from the switch to the polymer.

It would be tempting to make a comparison of the performance and reliability of various modifications of molecular opto-electrical switches in which the switching is triggered by photochromic reaction. In the authors' opinion, however, the experimental material gathered to date is scarce and incomplete, and much time and effort are necessary before such a comparison would be possible.

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