Contacts for organic switches with carbon-nanotube leads

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Abstract
We focus on two classes of organic switches operating due to the photo- or field-induced proton transfer (PT) process. By means of first-principles simulations, we search for the atomic contacts that strengthen diversity of the two swapped current–voltage (I–V) characteristics between two tautomers. We emphasize that the low-resistive contacts do not necessarily possess good switching properties. Very often, the higher-current flow makes it more difficult to distinguish between the logic states. Instead, the more resistive contacts multiply a current gear to a larger extent. The low- and high-bias work regimes set additional conditions, which are fulfilled by different contacts: (i) in the very low-voltage regime, the direct connections to the nanotubes perform better than the popular sulfur contacts, and (ii) in the higher-voltage regime, the best are the peroxide (-O–O-) contacts. Additionally, we find that the switching-bias value is not an inherent property of the conducting molecule, but it strongly depends on the chosen contacts.

Keywords: electronic contacts, photoswitches, fieldswitches, organic electronics

1. Introduction

Miniaturization caused mainly by energy savings, speed, and multi-functionality reasons is a strong driving force for molecular basic research. Diodes, transistors, switches, memory cells, and sensors are currently designed from molecular systems connected to metallic or carbon leads [1]. Fabrication of organic devices is technologically simpler, and its costs are lower. Thus, the search for organic substitutes for inorganic systems is a vigorous branch [2]. It is also dictated by ecological requirements, since in organic systems, the light atoms replace heavy—and toxic for the environment—elements. Moreover, the relatively new field of molecular electronics intensively stimulates the development of methods [3].

Metallic leads are widely used for nano-device electronics [4]; however, recently, carbon systems have become more popular [5]. This is mainly due to the better thermoelectric efficiency—which is a separate subject of investigations including vibronic effects [6–9]. Therefore, we decided to use carbon nanotube (CNT) leads. To date, carbon-system contacts to metal leads have been explored for C60 [10, 11], CNT [12, 13], and graphene [13, 14].

Various types of electrodes and nano-devices, as well as their functionalities, set requirements for electronic contacts [15, 16]. Their role was addressed a decade ago [17, 18], and it is still of major importance [3, 19]. All types of devices seek low-resistivity contacts in order to avoid large heat dissipation [20–22]. Additionally, some contacts are designed to be spin-selective [23]. Switches, however, need contacts which are low-resistive, and, additionally, that amplify the current gear obtained at the transition between two or more molecular forms, so that an effect of the switched logic state is easily measured in the circuit. Finding such contacts is the main goal of our study, since according to our knowledge it has not been addressed to date.

Molecular switches work under various external triggering stimuli: electric or magnetic field, light, temperature, chemical reaction, mechanical stress, radiation, etc [24]. Here, we focus on two classes of molecular switches, which operate under photo or field stimuli. The first group can operate at very low voltage, since the tautomeric transition is triggered by light, not by bias. The second group works in the wide range of voltages, set by the values of swapping biases which are different for the state-on and the state-off. These voltages
typically are higher than the low-bias regime in which the photoswitches operate. The higher-bias regime is more demanding for electronic contacts. Hence, it is much more difficult to obtain a high current gear for the field switches than for the photoswitches.

In this work, we used first-principles methods for the electronic structure and ballistic conductance calculations to obtain the current-voltage (I-V) curves the tautomeric switches connected to CNT leads. The studied photo and field switches are based on the proton transfer between the oxygen and the nitrogen centers [25–30]. The contacts are chosen among the light atoms or chemical groups: -C-, -C≡C-, -O-, -O-O-, -S-, -CS2-, -CH2-, and -NH-, as well as the direct connection to the CNT. Some choices might appear fancy at first sight; however, the results on a nanoscale are often surprising [31].

Interestingly, the switching voltages are not the properties of the conducting molecules only, but they depend strongly on the selected contacts. Among the investigated in this work structures, the cases with multiple negative differential resistance (NDR) show up, and they were described in our previous work as candidates for high-frequency devices [32].

2. Results and discussion

It is a common practice that sulfur contacts are used to connect a molecule to metallic or carbon-based leads. Some authors connect the molecule directly to the graphene surface or the carbon nanotube [33]. Here, we check some other possibilities. Among others, we explore the properties of acetylene (-C≡C-), oxygen (-O-), and peroxide (-O-O-) contacts. Generally, the oxygen element is not popular as a contact. But when oxygen is added to some conductive structures, it can bring along a new physics [34–36]. Below, we report the results for two types of molecular switches, triggered either by light or by voltage; both are based on the PT reaction along the intramolecular hydrogen-bond.

2.1. Photoswitches: low-voltage work regime

The photoswitches discussed in this subsection differ from the field switches discussed hereafter by the fact that their two photo-tautomeric structures form due to a reversible photo-induced intramolecular proton-transfer process, while the fieldswitching induces this reaction in the ground electronic state. Photo switching of molecular conductance is studied for the two stable isomers of salicylidene methylamine (SMA) [27, 28]. The photo-induced PT reaction occurs between the oxygen atom of the hydroxyl group and the nitrogen atom of the amino group of SMA [30]. Both respective photo-tautomeric forms—called the enol and keto—are presented in figure 1. Additionally, these forms differ from each other by the conformation of the methylamine tail with respect to the salicylidene core [27]. The importance of the contact geometry for transport properties has been shown for many systems [10, 37–40]. Moreover, the properties of the junction may also depend on the CNT chirality; thus, all carbon electrodes considered in this work are of the zigzag type—the most effective form for the switches [41].

Following the work by Staykov et al [30], we simulate transport in various structural connections to the leads: para, meta, and, not studied earlier, ortho—all displayed in figure 1. But our main aim is to check the switching impact of contacts, such as the direct connection, O, and S atomic connections. The S and O connections form angular structures with the CNT (about 105–120 degrees). In contrast, the direct connection is linear. Additionally, the electronic conjugation of the phenyl ring of SMA is extended by acetylenic moieties attached on its two sides, the so-called anchor groups. Former studies of these molecules framed, however, between the metallic electrodes have revealed that the meta connection is much more efficient for photoswitching than the para one [30]. In this work, we considered also the ortho structure. The
obtained $I$–$V$ curves are presented in figure 2. (Details of the calculations are given in the methods section.)

Focusing on the resistivity of the contacts and the connecting structures, generally it is not a surprising that the sulfur atom is the best conductive contact within the range of applied bias (about 2 V). The meta structures are much more conductive than the para, and also more than the ortho, with an exception that for the direct connection, the meta and ortho geometries show similar currents for the enol and keto structures below 2 V. Transition voltages, in the sense of the voltage at which the current rises from zero for very small applied biases [42], are usually lower for -O- than -S-, and are the lowest for the direct connection. This fact sets the working bias-regimes: $V_{\text{work (direct)}} < V_{\text{work (O)}} < V_{\text{work (S)}}$.

Further inspection of the results presented in figure 2 leads to the following conclusions: (i) The most interesting result with respect to the current gain between the two isomeric forms at very low bias, up to 0.4 V, is obtained for the cases of direct- and oxygen para and ortho, but it is not the case with the S contact; and (ii) For the voltage around 2 V, the best performing switches are: oxygen contacts and direct-meta, and S-meta and -ortho. For some cases, the negative differential resistance is observed—especially with the direct contacts. This effect, however, does not exclude the device from operation if we choose the proper working bias-range ($< 0.4–0.8$ V).

2.2. Field switches: higher-voltage work regime

The electric field applied to the molecule may tune the shape of the energetical landscape of the ground-electronic state, and thus it may change the relative stability of the two tautomeric forms of the molecule. One form which is the most stable without the E-field may become less stable or even unstable in the higher voltage values that favor another tautomeric form. In the studied case the enol form is the only stable form when no field is applied (see figure 3(a), black...
filled circles). To stabilize the keto form one must apply the electric field along the main axes of the molecule, which is also the direction of the proton transfer between the oxygen and nitrogen atoms that transforms enol into the keto form. Thus, the distance between the oxygen and hydrogen atoms, $R$(OH), is the best choice of a driving coordinate for an illustrative description of the process. To characterize the process in more detail, we construct the minimum-energy profile (MEP) along the driving coordinate. Along the MEP, all the intramolecular nuclear degrees of freedom are optimized for a given frozen value of the driving coordinate $R$(OH). Separate ground-state MEPs are calculated for different values of the electric field applied to the molecule. Bias values in volts are given in figure 3(a) above the corresponding MEP additionally distinguished with shape and color. Those indicate changes in the ground-state energy landscape: the heights of the enol-to-keto and keto-to-enol tautomerization-reaction barriers and the stabilization energy of both forms. MEPs plotted in figure 3(a) represent relative energy normalized at $R$(OH) = 1.4 Å.

Potential-energy profiles sketched in figure 3(a) result in a ‘hysteresis’ of the field-induced switching between the tautomeric forms of the 2PPy molecule terminated with the methyl groups. The hysteresis curve presented in figure 3(b) represents the minimum energy of a given tautomeric form normalized vs. the mean energy of both tautomeric forms (the zero-energy of the scale) at the applied value of bias. One can see that both tautomeric forms of 2PPy can coexist within a given range of the applied voltage, the terminal values of which define the limits $V_1$ and $V_2$, where the PT process enol-to-keto and keto-to-enol takes place, respectively. The switching values of the voltage impose the limits on the $I$–$V$ characteristics computed for a given tautomeric form (figure 3(c)). The operation mode of the device is as follows: we start from the enol form, and when the voltage is increased to the value higher than $V_1$, the molecule switches to the keto form. Then, the bias is decreased down to the second switching voltage $V_2$, and the reverse transformation to the enol form occurs. This effect shows up as a jump of the current flowing via the molecule (figure 3(c)).

Similarly to the photoswitches discussed above, and also for the field switches, different geometric connections to the CNT can be realized; they are presented in figure 4(a)–(d). In figure 4(e), we show the zigzag geometry of the peroxy (-O-O-) contact in contrast to the linear geometry of the acetylenic (-C≡C-) one. The contact via the CS$_2$ planar group is depicted in figure 4(f). It is interesting to explore the CS$_2$ group, since it has been announced as a very low-resistive contact for gold leads characterized by low electronic work-function [20, 43]. To complete these studies, we add also the -NS$_2$- connection to our list (in the same geometry as the -CS$_2$- contact). It has been experimentally evidenced that the field switching is a robust property of a molecule and not a stochastic phenomenon [44]. We show in this work that the switching effect is not only a property of the molecule but also strongly depends on the chosen contact. As one may notice inspecting figure 4, the single-branched contacts might be arranged to the 2PPy switch in the three-fold manner as ‘left,’ ‘right’- or ‘central’ configuration. The double-branched contacts were studied earlier by us and showed the negative differential resistance [32], which in some cases can exclude the system as a candidate for a switch.

In table 1, we collect the high, $V_1$, and the low, $V_2$, transition voltages determined for various contacts and structures presented in figure 4(a)–(d). For completeness, we also show the tautomeric switching biases for the bare molecule—not connected to the leads. Inspection of these results leads to the following conclusions: (i) The operating voltage range for a given tautomeric form, $V_1$–$V_2$, is relatively wide (several volts), and (ii) Various contacts and structures introduce large diversification of the work regimes. It is very important that the relatively large switching bias in some cases is perhaps too high for technological applications. It is generally more practical, for stability reasons, to utilize the device operating under a lower transition ($V_2$), although, in reality the theoretically predicted demands are overestimated.
The calculated barriers would be much smaller when the temperature, vibrational, interface, and tunneling effects were included [45]. Analyzing the results obtained for different connections presented in table 1, one may state that the double-branch and ‘right’-single-branch structures seem to be the most promising choice (smaller $V_2$), while the larger $V_2$ values are given for the ‘left’-single-branch connections, and the single-branch ‘central’ connections are characterized by the highest switching biases. On the other hand, as we will see hereafter, the latter case is the only non-NDR case that is stable with respect to switching.

The I-V curves computed for single-branch side connections, ‘left’ and ‘right,’ are depicted in figure 5. These curves correspond to the structures shown in figure 4(a)–(d). The NDR effect seen in some cases is very often detected in the triangular lattices, such as graphene and some organic molecules [46]. Here, we observe the NDR for the single-branch ‘left’- and ‘right’-side structures (figure 5), and this effect is even stronger than for the double-branch case [32]. This is generally an undesired effect with respect to the switching performance. Some remedy for this problem possibly could be found using longer anchor groups, since a suppression of the quantum conductance oscillations (leading also to the NDR effect) was reported [47]. On the other hand, the energetic barriers to be conquered in the course of the PT process are not very high (see figure 3(a)), and the vibrational or thermal effects may lower them, as mentioned earlier, thus moving the transitions to the next bias-point ($V_1$ to lower and $V_2$ to higher), narrowing the hysteretic loop, and shifting the operation region to the non-NDR part. The work regimes, chosen for the lower transitions at $V_2$, are marked in the I–V characteristics by dashed green lines. Despite the NDR effect existing in all cases in figure 5, the -NH- and -S- ‘left’-side contacts seem to be promising for technological applications due to a large gear of the enol and keto currents in the vicinity of the switching bias.

Finally, the single-branch central structures were analyzed with respect to their I–V properties; the results are presented in figure 6. One can notice, upon inspection of the figure, that the keto-to-enol transition was not found up to 15 V.

### Table 1. The enol-to-keto (E-K) tautomeric switching bias $V_1$ (in volts)—when the voltage increases—and keto-to-enol (K-E) switching bias $V_2$ (in volts) when the voltage decreases.

| Contacts          | $V_1$ | $V_2$ | $V_1$ | $V_2$ |
|-------------------|-------|-------|-------|-------|
| double-branch     |       |       |       |       |
| bare molecule(*)  | 6.2   | 2.6   | 9.7   | 4.3   |
| -CH$_2$-          | 5.4   | 1.4   | 10.3  | 5.4   |
| -NH-              | 7.2   | 2.9   | 10.1  | 5.3   |
| -S-               | 6.2   | 2.1   | 8.7   | 4.9   |
| direct(b)         | 8.9   | 3.1   | 15.9  | 5.6   |
| -C=O             | 11.5  | 5.7   |       |       |
| -CS$_2$(c)        | >15   | >15   |       |       |
| single-branch     |       |       |       |       |
| left              |       |       |       |       |
| -CH$_2$-          | 8.6   | 3.7   | 7.1   | 2.0   |
| -NH-              | 7.9   | 4.2   | 6.3   | 1.4   |
| -O-               | 7.7   | 4.1   | 7.7   | 2.4   |
| -S-               | 8.0   | 3.4   | 7.5   | 2.1   |
| right             |       |       |       |       |

* Molecule is ‘free-standing,’ not connected to leads.
* Molecule is directly connected to leads.
* The enol-to-keto transition was not found up to 15 V.

![Figure 5](image_url) 
*Figure 5. The I–V characteristics of the single-branch (left- and right-side) current-channels. CH$_2$, NH, O, and S were chosen for contacts X. Dashed vertical lines denote the bias at which the lower ($V_2$) tautomeric transitions occur; this is the measured current jump.*
values of the current. If the operating voltage range falls within the range where the characteristic parameters of the tautomers differ, then the current curves of the tautomers also differ.

The most important result of this section is the conclusion that for the peroxy (-O-O-) contact, a good current-gear for the switching at high voltage (∼ 5 V) is obtained. It is not an advantageous property of the peroxy contacts that they are more resistive than the acetylenic ones (-C≡C-). But the peroxy contacts strengthen the diversity of the conductances of different molecular structures—and this is what we need.

Since the sulfur contact is an electron-rich and highly polarizable moiety, the existence of an undesired NDR effect in this case is not surprising for larger biases [46]. We obtained nicely separated enol and keto current curves for -CS2- at voltages between 3.5–5.5 V. It is of little practical use, however, due to the fact that the switching voltage with increasing bias (V1) is for this contact higher than 15 V—up to the checked potential energy surface (see table 1), and we did not observe switching to the keto structure. Also the current values for the enol and keto forms show a tendency to join each other at biases higher than 6 V.

2.3. Transmission and the projected density of states

The electrical conductivity can be derived from the orbitals hybridization of the conducting molecule, atomic contacts, and the leads—those orbitals which energetically lay close to the Fermi level. Therefore, plots of the PDOS tell us about reasons for the existence of the quantum conductance peaks or their absence. Of course, not all states visible on the PDOS plots contribute to the current. In our systems, there are the lone electron pairs and the molecular orbitals that are orthogonal to the conduction direction. On the other hand, it is trivial that the lack of states in some energetic region results in no current.

In figures 7 and 8, we plot the quantum conductance (QC) and PDOS of photo- and field switches for selected contacts, for which the I–V curves were presented in figures 2 and 6. The electric fields at which the QC and PDOS plots have been obtained correspond to the bias 0.4 V and 2 V for the photoswitches (in figure 7) and 6 V for the field switches (in figure 8). For convenience, the corresponding values of the current (in microamps) are written in the top panels.

Transition voltage is the bias at which the current starts to grow from zero [42]. In the case of photoswitches operating at very low bias regime, the working voltages of the device are in the range where the enol and keto forms show different transition voltages. The lowest transition biases are for the direct contact, medium for oxygen and higher for the sulfur contacts. Following the discussion by Wu et al [42], the largest transition voltages are obtained for those atomic contacts whose 2p-states lay higher in the energy above the Fermi level. This is also true for the photoswitches and the PDOS presented in figure 7. The position of the 2p-states of the anchor group and the contact and the terminal carbon of the CNT lead are the highest in a case of the sulfur contact. For the direct contacts, these states are the closest to the Fermi level of all studied connections. The above sequence corresponds to the obtained current gears. The states which originate from the lonely pairs, or the orbitals non-overlapping with the conduction axis, do not contribute to the QC.

As for the resistance-related problems, it has been stressed in many reports—for instance, in the recent work by Schulz et al [20]—that the Fermi-level mismatch of the conductor and leads is responsible for the low conductance. Actually, for a good switch, one tautomeric form should be very resistive and the other well conducting in the device-operating bias region. In contrast to the bias regime of 0.4 V (upper panels), for 2 V (lower panel) the best performing contact is that with sulfur, and the next of oxygen. The low transition bias of the direct contacts does not work for the switch in the higher voltage range. This is because all PDOS diversities of the enol and keto forms are summed up to similar values when the bias range is larger. Instead, for the oxygen and sulfur contacts, not all PDOS mismatches between two tautomers appear in the bias range of 2 V.

For the field switches operating at higher voltages—around 5–6 V—the situation is more difficult. One needs to find contacts such that the nonsymmetric contributions to the PDOS from the tautomers do not sum up in the QC to similar values of current. In a case of the -C≡C- contacts, the quantum conductance spectra of tautomers are nonsymmetric but sum to similar currents (see figure 8). On the other hand, the nonsymmetric QC spectra of the peroxy contacts give a

![Figure 6](image-url)
good current gear. After inspection of the PDOS in the range of $[-3, 3]$ eV, the intensities of the acetoxy states are much smaller than the states of the peroxy case. Therefore, the tautomeric diversity is strengthened in the peroxy-contacts case, and they are the only contacts—of all studied here—which could work for the field switches.

Since the energetic positions of the contact states are very important, we emphasize that the simple density functional theory (DFT) method does not reproduce them well. One should go beyond this approximation, and, for instance, the self-interaction corrections and the constrained DFT method have been applied for the effect of the hydrogenation on the

Figure 7. Transmission functions of the photoswitches with the direct, -O-, and -S- contacts, obtained at bias 0.4 V (upper panels) and 2 V (lower panels); the enol is marked in black upside and keto in red downside. Numbers are values of the current (in $\mu A$) at 0.4 V and 2 V, respectively, from figure 2. PDOS of the $2p$-states of the anchor CC-group, the contacts, and the CNT terminal carbons connected to the contacts.
sulfur contacts in the BDT-gold molecular junction [48]. On the other hand, our leads and conductors are mainly carbonic, and not metallic. In contrast to the large underestimation of the energy gap in diamond by a simple DFT scheme, the carbonic conductive systems, such as graphene and CNTs, are well described within this method—the same as the band structures of simple metals. The DFT failure very strongly shows up when the metallic and non-metallic elements are combined, and the localized atomic-like $d$-states (or $f$-states) form. The relative position of these metallic states, with respect to the $sp$-states of the non-metallic atoms, is usually placed too shallowly below the Fermi level (or the highest occupied molecular orbital level). Similarly, the corresponding energies of the unoccupied metallic-states reside too low above the conduction band minimum (or the lowest unoccupied molecular orbital level). Such a situation leads to large overestimation of the calculated conductance. The systems studied in this work are purely non-metallic; therefore, they are free of the above-described mismatch of the two kinds of energy levels.

Since in this work we studied an impact of the geometry on the current, another interesting phenomenon could be addressed in a future work—namely, the current-driven geometric and electronic structure rearrangements. These effects would lead to nonlinear conduction characteristics and different switching properties. Such studies within the time-dependent Ehrenfest formalism were reported for the metallic clusters [49].

### 3. Conclusions

We searched for electronic contacts that strengthen the switching properties of molecular devices based on the intramolecular proton transfer process. Two classes of model molecular photo- and field switches, operating at lower- and higher-bias work regimes, respectively, were analyzed. By means of first-principles electronic calculations, we found the electronic structure, Wannier functions, and the electronic transport properties (the $I$–$V$ curves).

The larger the difference between the currents of the swapped structures, the better the performance of a switch. Moreover, we would like to have low-resistive contacts, but the mechanism of the current on-off switching with applied bias and the rules governing resistance stay in opposition to each other. It is demonstrated that for very low- and higher-bias work regimes, the efficient contacts are chosen according to different effects: (i) the transition voltage for the current-on switch and (ii) the resistive conformational selectivity, respectively. The low-bias operating range ($\sim$0.5 V) of photoswitches prefers the direct connection with leads, which is low-resistive. For the middle-voltage work regime (1–2 V), oxygen or sulfur are the best atomic contacts. The high-bias operating range ($>4$ V) of the field switches chooses the peroxo contacts.

In addition, we found that the transition voltages of the field switches are very sensitive to the choice of contacts. This is caused mainly by differences in the polarizabilities of the atomic contacts.

### 4. Methods

We performed the DFT [50] calculations of the molecules between the CNT leads using the plane-wave Quantum ESPRESSO code [51]. These self-consistent runs were repeated for many discrete external electric fields with a step visible in the reported figures. Then the obtained Bloch functions were used to generate maximally localized Wannier functions [52, 53] employing the wannier90 [54] code. The same package was then utilized for the transport calculations within the Landauer–Büttiker scheme [55]. The obtained QC (or transmission) for each electric field, $T(\varepsilon; E \sim V)$, was embedded in the equation [56]

$$I(V) = \int \left[ f(\varepsilon - \varepsilon_F + V/2) - f(\varepsilon - \varepsilon_F - V/2) \right] T(\varepsilon; E)d\varepsilon$$

with the Fermi–Dirac distribution $f(\varepsilon)$. This way, we reach the current $I$ at the bias $V$, which is equivalent to the external electric field $E$ assumed in the DFT calculations.

To estimate the voltage values necessary to switch the transistor forms, the enol to the keto and back to the enol, we optimized the geometry of the molecule at discrete values of the applied electric field (with the step of 0.001 a.u.). The DFT method implemented in TURBOMOLE [57] was used in these calculations along with the B3LYP functional and correlation-consistent valence double-zeta atomic basis set with polarization functions for all atoms (cc-pVDZ) [58] for a thoroughly studied exemplar PPy molecule terminated with methyl groups. For all other PPy derivatives the default def-SV(P) basis set was used in search of their characteristic $V_1$ and $V_2$ switching bias values.

#### Figures

**Figure 8.** Transmission functions of the field switches in the single-branch central geometry with the contacts $\text{-C}\equiv\text{C}$ (CC) and $\text{-O-O}$ (OO), obtained at bias 6 V; the enol is marked in black upside and keto in red downside. Numbers are values of the current (in $\mu$A) at 6 V from figure 6. PDOS of the $2p$-states of the CC and OO contacts and the CNT terminal carbons connected to the contacts.
As for the plane-wave calculations setup, the BLYP functional was used. The energy cutoff for the plane-waves in the Quantum ESPRESSO code was set to 30 Ry, and the pseudopotentials were of the Martin–Troullier type from the Fritz–Haber Institute library. In the QC calculations, each lead was built by the two CNT units, and the conductor region included the molecule with the contacts and one CNT ring saturated with hydrogens on the left- and right-lead side. The figures representing the molecular geometry have been prepared with the XCRYSDen package [59].

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