Switching the Conductance of a Molecular Junction using a Proton Transfer Reaction

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Abstract

A novel mechanism for switching a molecular junction based on a proton transfer reaction triggered by an external electrostatic field is proposed. As a specific example to demonstrate the feasibility of the mechanism, the tautomers [2,5-(4-hydroxypyridine)] and {2,5-[4(1H)-pyridone]} are considered. Employing a combination of first-principles electronic structure calculations and Landauer transport theory, we show that both tautomers exhibit very different conductance properties and realize the “on” and “off” states of a molecular switch. Moreover, we provide a proof of principle that both forms can be reversibly converted into each other using an external electrostatic field.

Introduction

Molecular junctions, where a single molecule is bound to two electrodes, provide interesting systems to study basic mechanisms of non-equilibrium charge transport at the nanoscale and are promising candidates for the development of nanoelectronic devices. The possibility of using single molecules as electronic components in electronic circuits has motivated intensive experimental and theoretical research on the conductance properties of these systems and revealed a multitude of interesting transport phenomena. In particular, it has been demonstrated that a molecular junction may be used as a nano switch if the molecule bridge has two (or more) stable states with different conductance, which can be reversibly transformed into each other.

In recent years, several optical and non-optical mechanisms for molecular switches in junctions have been investigated. Many of the optical mechanisms rely on conformational changes of the molecule triggered by light absorption (such as light induced cis-trans isomerization processes) to facilitate reversible switching between different conductance states. Non-optical mechanisms investigated include electrochemical switching, where a reversible redox pair is generated using voltage pulses or mechanical switching, where external mechanical forces are applied to produce the reversible change between states with different conductance.

In recent theoretical work by some of the authors, it was shown that it is possible to use...
a photoinduced excited state hydrogen transfer reaction between the keto and enol tautomers of a molecule to realize a molecular switch. As was demonstrated for an example of a polyene functionalized with keto and amino groups, this switching mechanism relies on the fact that keto and enol tautomeric forms often exhibit different conjugation properties, which are associated with localized or delocalized charge distributions on the molecular bridge, and thus realize different conductance states.

In this contribution, we build on these results and propose a new non-optical switching mechanism based on a ground state proton transfer reaction triggered by an external electrostatic field. As an example to demonstrate the feasibility of this mechanism, we study the ground state proton transfer reaction between oligomeric forms of p2HP and p2PY. Specifically, we investigate the proton transfer reaction between the enol tris[2,5-(4-hydroxypyridine)] (T2HP) and the corresponding keto form tris{2,5-[4(1H)-pyridone]} (T2PY) (for binding to the Au leads, the oligomers have been appropriately functionalized at their ends as indicated in Fig. 1). We show that both tautomers exhibit different current-voltage characteristics providing the “on” and “off” states of a molecular switch and provide a proof of principle that both forms can be reversibly interconverted using an external electrostatic field.

**Methods**

To investigate the transport properties of the molecular junctions, we have used a methodology which combines electronic structure calculations employing density functional theory (DFT) and Landauer transport theory. The method has been described in detail previously. Here, we only provide the main aspects and some details specific to the current application.

In the electronic structure calculations, we have modelled the molecular junction using the bridge molecule and two clusters containing three layers of Au atoms (comprising a total of 88 Au atoms). The equilibrium structures of the keto and enol tautomers have been optimized using DFT methods. Specifically, as described elsewhere, we have carried out a partial geometry
Figure 1: Keto tris{2,5-[4(1H)-pyridone]} (T2PY, top) and enol tris[2,5-(4-hydroxypyridine)]
(T2HP, bottom) tautomers of the molecular switch investigated in this work. Both forms have
been functionalized for binding to the Au leads with 3,4-dimercapto-(1H)-pyridine and 3,4-
dimercapto benzenone (keto form, top) and 3,4-dimercaptopyridine and 3,4-dimercaptophenol
(enol form, bottom).

optimization of a cluster consisting of the respective tautomer and the first layer of the Au atoms
of each lead in order to determine realistic tautomer-lead binding geometries. Subsequently, two
extra layers of Au atoms per lead were added to the optimized structures to obtain the models
investigated in this work (see Fig. 1). Following previous work\textsuperscript{35}, all calculations were carried
out using the B3LYP hybrid correlation-exchange functional together with a SV(P) basis set\textsuperscript{38}
(Au atoms have been described using the ECP-60-MWB pseudopotential\textsuperscript{39}) as implemented in
TURBOMOLE\textsuperscript{40}. To describe the effect of infinite leads we have added the surface self-energy of
a Au(111) surface to the atomic orbital energies of the Au atoms of the outer layer of both leads.\textsuperscript{35}

The current for a given voltage was obtained from the Landauer formula\textsuperscript{41}

\[
I = \frac{2e}{h} \int T(E) \left[ f_L(E) - f_R(E) \right] dE
\]

where \(f_L(E)\) and \(f_R(E)\) are the Fermi distributions of the left and right lead, respectively,\textsuperscript{42} and
\(T(E)\) is the transmission function, which depends on the applied bias voltage. \(T(E)\) contains the
information about the junction and can be expressed as

\[ T(E) = \text{tr}_M[\Gamma_L(E)G_M^\dagger(E)\Gamma_R(E)G_M(E)] \]  

(2)

Here, \( G_M(E) \) denotes the molecular Green’s function and the functions \( \Gamma_{L/R} \) describe broadening of molecular states due to coupling with the metallic leads. The methodology to obtain these functions is described in Ref. [36]

**Results and Discussion**

Fig. 2 shows the current-voltage characteristics calculated for T2HP and T2PY (see Fig. 1). The results reveal very different transport properties of the two tautomers. While the keto form exhibits a rather low current, the enol form facilitates a significantly larger current for bias voltages \(|V| > 0.5 \text{ V}\). Thus, for a given bias voltage, the two tautomers realize different conductance states of the molecular junction and can be associated with “on” (enol) and “off” (keto) states of a molecular nano switch.

To obtain insight into the mechanism underlying the very different conductance properties of the two tautomers, we have analyzed their transmission functions \( T(E) \) (see eq. (2)), depicted for zero bias voltage in Fig. 3. The current is determined by the values of the transmission function close to the Fermi energy. Both tautomers exhibit low values of transmission in the immediate vicinity of the Fermi energy resulting in low current for bias voltages \(|V| < 0.5 \text{ V}\). Significant values of transmission are observed for energies \(-1.5 \text{ eV} < E < -0.5 \text{ eV}\), below the Fermi energy. The structures of the transmission function in this energy range reveal a pronounced difference between the two tautomers. In particular, the transmission peaks of the enol form are significantly broader, indicating a stronger coupling of the molecular bridge to the leads and, thus, resulting in the larger current observed for bias voltages \(|V| > 0.5 \text{ V}\) (cf. Fig. 2). This finding is corroborated by an analysis of the molecular orbitals associated to the most relevant structures in the transmission function, depicted in Fig. 4. In the case of the enol form, the peak at \( E = -1.25 \text{ eV} \) is associated
to the \(\pi\)-like orbitals (a) and (b) that extend over the molecule. On the other hand, the orbital (c) in Fig. 4, which is responsible for the peak at \(E = -1.4\) eV in the keto tautomer, is more localized and has most of its density in the center of the molecule. The difference in the extension of the orbitals of the enol and keto forms can be explained in terms of the degree of conjugation present in both systems. Whereas the enol form is mainly characterized by a delocalized valence bond structure, the contribution of this class of valence bond structures to the keto tautomer can be expected to be less important.

The results presented above suggest that T2PH and T2PY may be used as the “on” and “off” states in a molecular nano switch. To achieve this functionality, a mechanism for a reversible transformation between the two tautomers, i.e. a proton transfer, is required. For this purpose, the different charge distributions of the two tautomers may be exploited. As is well known, proton transfer reactions may be triggered by an external electrical field. To investigate this possibility, we have studied the relative stability of both tautomers in the presence of a constant external electrostatic field oriented in a direction along the axis of the junction (see Fig. 5). As a measure
of the relative stability of the keto and enol forms, Fig. 5 depicts the difference of their ground state energies as a function of the strength of the applied external field. The results show that without external field, the most stable tautomer is the enol form. This is due to the stabilization obtained by aromaticity and conjugation. Application of an external electric field modifies the situation. Upon a gradual increase in the strength of the field the energy difference between the enol and the keto forms decreases and for values larger than \(4.73 \times 10^9\) V/m an inversion of the relative stabilities of the tautomers can be obtained. This provides a proof of principle that a reversible interconversion between the T2HP and T2PY using an external electrostatic field is possible. In a more general context, the possibility to control the conductance by an external electrostatic field, may also be used as a mechanism for a single molecule transistor.

We finally mention some possible extensions of the present study. First, for the specific system investigated, the largest difference in current occurs only for larger voltages. This is due to the fact that the most relevant molecular orbitals have energies further away from the Fermi energy. An optimization of the functionality can thus be achieved by using chemical substitutions that shift...
Second, in the present study we have focused on the conductance properties of the two tautomers at fixed nuclear geometry. An investigation of the mechanism of switching requires the modelling of the potential energy surfaces along the reaction coordinates and the nuclear dynamics under bias. Third, the external electrostatic field may also influence the conductance, e.g. by shifting the energy levels of the molecular bridge. Thus a more complete description has to include the electric fields of the junction and the external electric field in the transport calculations. This will be the subject of future work.

Conclusions

We have explored the possibility to use a proton transfer reaction as a mechanism for switching a molecular junction between different conductance states. As a specific example, we have analyzed the conductance properties of T2HP and T2PY enol-keto tautomers. We have shown that both forms exhibit very different electrical currents, which allows their use as the “on” and “off” states of a molecular nano switch. The origin of this difference has been explained in terms of the different electronic structures characterizing both tautomers. Furthermore, we have demonstrated that switching between the two conductance state may be achieved by an external electrostatic
Figure 5: Energy difference between T2PY and T2HP for different values of the applied external electrostatic field. The inset shows the direction of the field.

field which triggers a proton transfer reaction that interconverts the two tautomers reversibly. The results of this theoretical study suggest that keto-enol tautomers can be used as building blocks of a nanoscale molecular switch or, more generally, a molecular transistor.

Acknowledgement

This work has been supported by the German-Israeli Foundation for Scientific Development (GIF), the Deutsche Forschungsgemeinschaft (DFG) through the Cluster of Excellence “Engineering of Advanced Materials” (EAM), SFB 953 and a research grant, as well as projects, CTQ2012-36966 (MICINN), and UAH2011/EXP-041 (UAH). ALS acknowledges the research grant of the National Science Centre of Poland 2011/01/M/ST2/00561. Generous allocation of computing time at the computing centers in Erlangen (RRZE), Munich (LRZ), and Jülich (JSC) is greatly acknowledged.
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