

# Interference effects in phthalocyanine controlled by H-H tautomerization: Potential two-terminal unimolecular electronic switch

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(Received 23 March 2011; revised manuscript received 26 September 2011; published 21 October 2011)

We investigate the electrical transport properties of two hydrogen tautomer configurations of phthalocyanine ( $H_2Pc$ ) connected to cumulene and gold leads. Hydrogen tautomerization affects the electronic state of  $H_2Pc$  by switching the character of molecular orbitals with the same symmetry close to the Fermi level. The near degeneracy between the HOMO and HOMO-1 leads to pronounced interference effects, causing a large change in current for the two tautomer configurations, especially in the low-bias regime. Two types of planar junctions are considered: cumulene- $H_2Pc$ -cumulene and gold- $H_2Pc$ -gold. Both demonstrate a prominent difference in molecular conductance between ON and OFF states. In addition, junctions with gold leads show pronounced negative differential resistance (NDR) at high bias voltage, as well as weak NDR at intermediate bias.

DOI: [10.1103/PhysRevB.84.165437](https://doi.org/10.1103/PhysRevB.84.165437)

PACS number(s): 73.63.-b, 85.65.+h, 31.15.E-, 07.60.Ly

## I. INTRODUCTION

The ability to control current in molecular junctions is a prerequisite for functional devices in molecular electronics. Of particular interest for nanoelectronics are two-terminal switches characterized by two distinct current-voltage characteristics (IVCs) representing ON and OFF states, switchable by exceeding threshold voltages in hysteretic junctions. With such two-terminal components one can in principle build nanoscale memory and resistor-diode logic for scalable architectures.<sup>1,2</sup>

A major challenge is to develop two-terminal unimolecular switches (UMS) where the switching is truly intramolecular, and not due to cooperative or interface effects in multimolecule junctions. One UMS example is provided by a recent experiment by Lörtscher *et al.*, using a mechanically controlled break junction (MCBJ) to demonstrate switching and hysteretic IVCs of a single Tour-wire molecule.<sup>3,4</sup>

A UMS should be electrically coupled and immobilized in the circuit, yet have enough freedom to perform switching. Up to now, several different kinds of molecular switches have been proposed, most of them involving a change of molecular conformation<sup>5-7</sup> or redox state.<sup>8</sup> An interesting case related to the present discussion is the SnPc switch,<sup>9</sup> where the current is determined by the vertical position of the tin atom, controlled by a scanning tunneling microscope (STM).

Recently, Liljeroth *et al.*<sup>10</sup> proposed a new type of molecular switch where the switching is mediated by a tautomerization reaction of metal-free naphthalocyanine. Using a low-temperature STM, a voltage pulse at the STM tip can induce a change in the orientation of the hydrogen atom pair at the center of naphthalocyanine, leading to switching between low and high conductance. The fact that naphthalocyanine does not change position or conformation of the molecular framework could be very beneficial for controlling molecular electronic circuits. If the molecule can be integrated in the circuit, it will not move or change its outer shape upon switching.

There are now a variety of techniques that can be used for contacting and investigating single molecules (see, e.g.,

Refs. 11–21). However, when it comes to interconnecting single molecules to functional electronic circuits, there are currently no working solutions. The circuits will necessarily have to be based on various forms of self-assembly of building blocks,<sup>22,23</sup> but the field is wide open, and extensive fundamental research will be needed before useful functional systems can emerge.

One possibility to wire circuits could be to first deposit the molecules and then grow the wires. This case has recently been investigated by Okawa and co-workers,<sup>24–26</sup> with the pronounced goal to fabricate a single-molecule integrated circuit. Nanoclusters of phthalocyanine molecules are adsorbed on a molecular layer of diacetylene, and chain polymerization is initiated by applying a pulsed bias voltage to the row of diacetylene molecules to which a phthalocyanine pentamer is adsorbed. In this way Okawa *et al.*<sup>26</sup> recently succeeded in connecting two polydiacetylene chains to the same pentamer phthalocyanine molecule.

In this paper, we focus on the planar electrical transport properties of a UMS based on hydrogen tautomerization in metal-free phthalocyanine ( $H_2Pc$ ) connected to semi-infinite metallic wires of carbon (cumulene)<sup>27</sup> or gold. The transport properties are examined as a function of the electronic structure of the tautomer state of the molecule, the type of leads, and the coupling between electrodes and the molecule. Our results show that switching the orientation of the H-H atom pair in the  $H_2Pc$  cavity can significantly change the conductance of the molecule, effectively leading to ON and OFF states for both cumulene (Fig. 1) and gold (Fig. 2) leads. Moreover, in the case of gold we find that negative differential resistance (NDR) appears at high bias voltages due to reduced transmission through one of the contacts.

A few important clear limitations should be noted from the start: we treat neither (i) the influence of any substrate nor (ii) the switching mechanism and stability (usefulness) of the switch. Liljeroth *et al.*<sup>10</sup> have demonstrated experimentally that the switch works in principle in vertical transport (STM)