



Original research article

First-principles study of the electronic transport properties of a 1,3-diazabicyclo[3.1.0]hex-3-ene molecular optical switch



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ABSTRACT

We analyze the transport properties of 4-(6-(4-chlorophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)-2-nitrophenol molecular optical switch using first-principles calculations. Molecule consisting switch can transform among closed and open forms by visible or ultraviolet irradiation. We have studied multiple attributes such as I–V characteristics, electronic transmission coefficients $T(E)$, the effect of electrode materials (Au, Ag, and Pt) on electronic transport properties, on-off ratio and spatial distribution of molecular projected self-consistent Hamiltonian (MPSH) orbitals corresponding to the closed and open forms. The physical origin of switching behavior is interpreted based on the different molecular geometries, location and size of the frontier molecular orbitals and the HOMO–LUMO gap. According to the theoretical results, one can find that when the open form converts to the closed form, there is a switch from low resistance (on state) to high resistance (off state). We hope that the results of this study can help researchers to design new functional molecular devices.

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1. Introduction

Photochromism is a phenomenon in which a compound follows reversible changes between two states with different absorption spectrums such that different colors are created from compounds in crystal, amorphous or liquid states. Under electromagnetic radiation (usually UV light), stable thermodynamic shape A transforms to a new colorful type B via photochemical reaction and type B changes to the initial shape A on reverse direction via another light source like visible light or heat [1–4]. Photochromism delivers a suitable insight to the expansion of optical sensing applications [5], high-density optical memory [6], photo-switches [7], molecular photonic devices [8] and light-sensitive eyewear [2]. The photochromism of 4-(6-(4-chlorophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)-2-nitrophenol is shown in Fig. 1 [9]. Also, photochromic behavior can be observed when the 1,3-diazabicyclo[3.1.0]hex-3-ene connect to the silver [10].

Recently, a lot of interesting physical properties such as highly nonlinear I–V characteristics, memory effects, negative differential resistance (NDR), switching properties, electric rectification behavior and etc. are found in various systems such as organics [11], DNA [12] and carbon nanotubes [13]. The supreme aim in microelectronic crafts is the perpetual miniaturization of electronic devices and the final target is to synthesize devices by using a molecule, a cluster or even an

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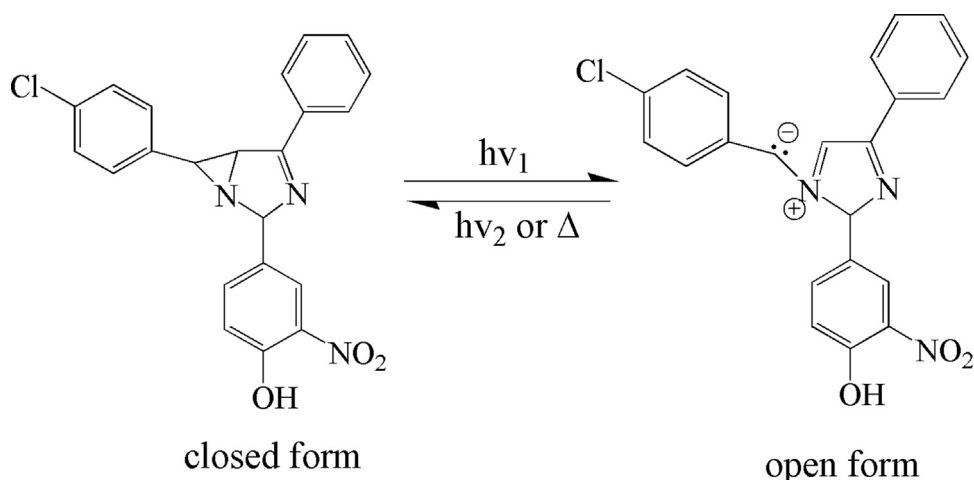


Fig 1. Chemical structures corresponding to closed and open form of the 4-(6-(4-chlorophenyl)-4-phenyl-1,3-diaza-bicyclo[3.1.0]hex-3-en-2-yl)-2-nitrophenol.

atom [14–16]. Lately, synthesis, design and investigation of photochromism molecular switches of effective components in nanoelectronics research, become a research hotspot. Meantime, the computational researches of photochromism molecular switches, adopting to first-principles methods have also attracted growing considerations [16,17].

Wide areas of molecular switches have been published in the literature [18–20], with bistable and high/low conductance forms which are activated by several types of external motivations [21–23]. Among those, light is a very attractive stimulus due to its quick response time, feasibility of addressing, a wide range of condensed phases and compatibility with already existing experimental setups [20,24]. According to this, azobenzene- and diarylethene-based photochromic switches have been investigated, comprehensively [16,25–29]. Generally, due to light treatment, molecular optical switches involve changes in the molecular structure such isomerization reactions of the molecular bridge and ring-opening reactions.

Newly, we have described another mechanism which is based on solvent induced hydrogen shift in molecular bridge [30]. Also in previous work, 2-([1,1'-biphenyl]-4-yl)-2-methyl-6-(4-nitrophenyl)-4-phenyl-1,3 diazabicyclo [3.1.0]hex-3-ene photochromic switch has been studied [31]. The closed form of switch can be transformed into the open one upon irradiation with 300 nm ultraviolet light (UV) which results in increasing the magnitude of conductivity by 10^3 . These two forms can survive in a wide temperature range and can reversibly change to each other, which make the title compound as an excellent candidate for light-driven molecular switches. In this project, Non-equilibrium Green's function (NEGF) formalism merged with first-principles density functional theory (DFT) were used to study the conductive behavior of the switch of the title compound.

2. Model and computational methods

In the present work, the calculations are done in two steps. In the first step, geometry optimization of 4-(6-(4-chlorophenyl)-4-phenyl-1,3-diaza-bicyclo[3.1.0]hex-3-en-2-yl)-2-nitrophenol with one SH group as linker is performed by Gaussian 03 program [32] with B3LYP type exchange correlation functional [33] and the popular 6-311++G(d,p) basis set [34]. Positive values of all calculated vibrational wave numbers certified the location of geometries at real positional least minimum on the potential energy surface.

Chlorine atom can be easily attached to metal [35], but it is generally accepted that hydrogen atoms are unzipped upon adsorption to metal surfaces [36,37]. So we construct a two-probe system in which the one terminal hydrogen atom that bonded to the sulfur atom is deleted from the optimized structure, and the remained segment is located between two parallel metal surfaces. It's both closed and open forms have one S-linker and are connected into the Gold junction with (1 1 1) surfaces. The modelled molecular connection structure is illustrated schematically in Fig. 2. The central section involves sections of the electrodes, so the screening results can be included in computations.

The most common X (1 1 1) surface [38,39] is used with (6 × 6) periodic boundary conditions. The 6 × 6 supercell is big sufficient to avoid any interplay with molecules in the subsequent supercell [30,31]. The sulfur and chlorine atoms are elected to place at the hollow location of the X triangle. Since the main purpose of this work is to determine the switch of conductivity through a photochemical reaction, the nature of Au–S interaction is not investigated here. The vertical distance between the sulfur and chlorine atoms with X (Au, Ag and Pt) surface are set to be 1.9, 2.0, 2.4 Å and 2.3, 2.7, 2.8 Å, respectively [35,40–43].

The core electrons are modelled with Troullier–Martins nonlocal pseudopotential [44], while the valence electrons wave functions are expanded by a SIESTA basis set [45]. Since transport properties are going to be calculated after the structural relaxations, only atoms in the scattering region are fully relaxed within a force convergence criteria of 0.02 eV/Å, while

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