Front. Phys. 12(4), 127303 (2017)
DOI 10.1007/s11467-016-0623-0

RESEARCH ARTICLE

Frontiers of Physics

Conductance switching of a phthalocyanine molecule on an insulating surface

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Received August 31, 2016; accepted September 8, 2016

We study the electron transport through the double-barrier junction consisted of the phthalocyanine molecule adsorbed on a NaCl bilayer on a metal substrate and the STM tip from first principles. The hydrogen tautomerization reaction happened in the molecule changes the spatial extensions of the molecular π orbitals under the tip, leading to junction conductance switching. Shifting the molecule to locate on different ions also varies the conductance. The transport channels of the tautomers on different adsorbed sites are identified.

Keywords first-principles calculations, double-barrier junction, NaCl bilayer, tautomerization, molecular electronics

PACS numbers 73.63.-b, 73.23.-b, 73.20.-r, 73.43.Jn

1 Introduction

In the past decade, various functional molecular components have been proposed and explored for applications in nanoelectronics [1–3]. Clearly, developing molecular switches is the focus of researches along this line. Rather than involving drastic conformational changes in the molecule [4, 5], molecular switches based on porphyrins and related macrocycles anchored to a surface [6–8] have a central cavity that can incorporate two hydrogen atoms to form two-level states. Tunneling electrons from the STM tip can trigger the transfer of hydrogen atoms within the cavity (known as tautomerization) to switch between states, without altering the molecular frame [7, 8], so that the coupling between the molecules can be well controlled. These key molecules, however, have to be well separated from the metal substrate to fully accept the energy of tunneling electrons [9]. Adopting the tetraphenyl-porphyrin molecule which can stands out from the surface, the four-level conductance switching is observed [7]. Adsorbing the naphthalocyanine molecule on an ultrathin insulating surface, the high and low currents are read out [8].

In view of first-principles computational modellings, the result of the naphthalocyanine molecule has been simulated, with the Tersoff-Hamann approximation [10]. On the other hand, conductance of a magnesium porphine molecule on a NaCl bilayer has been calculated based on density functional theory (DFT) and the nonequilibrium Green's function (NEGF) formalism [11]. However, conductance of a phthalocyanine molecule on an insulating surface is still not well addressed computationally to date.

In this work, we investigate the electronic transport through the double-barrier junction consisted of the phthalocyanine molecule adsorbed on a NaCl bilayer on an Au substrate and the tip by first-principles calculations. We find that the hydrogen tautomerization in the phthalocyanine molecule switches conductance values, as spatial extensions of the molecular π orbitals are altered. Changing the adsorbed site of molecule to different ions also varies the conductance. The transport channels of two tautomers on different adsorbed sites are identified.

2 Models and method

The junction model is schematically shown in Fig. 1. A slab structure is adopted to simulate the substrate, which consists of a NaCl bilayer (25 atoms per layer) and an Au (111) bilayer. Two semi-infinite Au (111)

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*Special Topic: Recent Progress on Quantum Transport in Nano and Mesoscopic Systems (Eds. Qing-Feng Sun, Zhen-Hua Qiao & Xin-Qi Li).

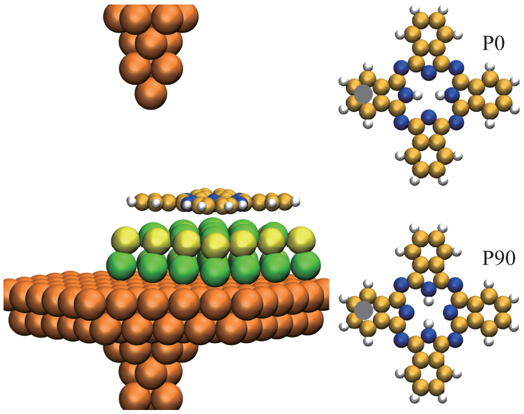

Fig. 1 Schematic of the molecular junction. Left: The slab consisted of a NaCl bilayer and an Au (111) bilayer with a nanowire for simulating the substrate. Right: Hydrogen tautomers. The tip locations are denoted by gray dots. There are gold (*dark orange*), chlorine (*green*), sodium (*yellow*), nitrogen (*blue*), carbon (*bright orange*) and hydrogen (*white*) atoms.

nanowires act as the top and bottom electrodes to reduce computational cost [11–13]. Phthalocyanine tautomers, P0 and P90, are adsorbed on the NaCl bilayer under the tip, forming double-barrier junctions. To investigate the electronic coupling between the molecule and the NaCl upper layer, only these two parts were relaxed using DFT implemented in the SIESTA package [14] and other atoms were fixed. The initial distance between the tip apex atom and the molecular plane was about 5 Å. Optimization calculations were performed within generalized gradient approximation (GGA) [15], with an energy cut off of 400 Ry. Valence electrons were expanded in double-ζ plus polarization for the NaCl bilayer and the molecule, and in single-ζ for Au electrode atoms, respectively. Structural relaxations were allowed until the force acting on each atom was less than 0.05 eV/Å. Then transport calculations were performed with Nanodcal package [16, 17], based on DFT and the NEGF formalism. The Brillouin zone was sampled by 100 k-points along the transport direction for the electronic structure of the Au electrode. The linear combination of atomic orbital basis-set, GGA and norm-conserving pseudopotentials were also used. The conductance value $G = T(E_\mathrm{f})G_0$, where $T(E)$ is the transmission spectrum, E_f is the Fermi energy, and $G_0 = 2e^2/\hbar$ is the conductance quantum.

3 Results and discussion

Since the molecule can be moved by the STM tip, two adsorption sites of the phthalocyanine molecule on the NaCl bilayer are considered: the molecular center on the Cl ion and on the Na ion. We address the former case first. The calculated conductance of P0 ($3.74 \times 10^{-7} G_0$) is higher than P90 ($2.97 \times 10^{-7} G_0$), while P90 is energetically favored (by 0.20 eV). Figure 2(a) shows the transmission spectra, where the transmission coefficient of P0 is higher than that of P90 in the energy window between −0.012 eV and 0.012 eV. Figures 2(b) and (c) plot the projected density of states (PDOS) of the molecule and the upper layer of NaCl, respectively. PDOS of the NaCl upper layer in the P0 junction is slightly higher than those in the P90 one at E_f, but PDOS of the molecule are reversed in those junctions. To demonstrate the transmission channel, it is helpful to investigate the evolution of local density of states (LDOS) of the molecule at E_f. Although the contour of LDOS, along the molecular plane, of P90 is stronger than that of P0, as shown in Figs. 2(d) and (g), the spatial extension of the molecular π orbitals towards the NaCl substrate should be more important for conduction. The contour of LDOS, along the molecular horizontal axis, of P0 is stronger than that of P90, shown in Figs. 2(e) and (h). The LDOS contours along the molecular vertical axis, shown in Figs. 2(f) and (i), are reversed. Since the tip locates at the molecular horizontal axis, the LDOS along this axis dominate the junction conduction. This conduction trend correlates with the coupling strength between the molecule and the tip, $\Gamma_{\mathrm{m-tip}}$, [11] of P0 (4.01×10^{-3} eV) and P90 (3.77×10^{-3} eV) junctions.

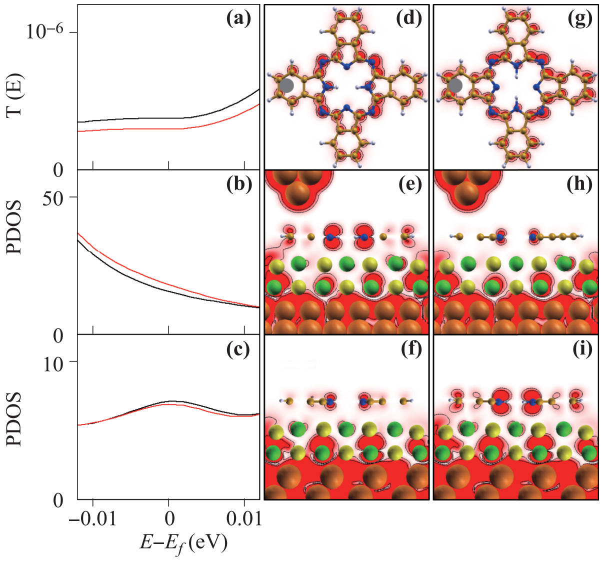

Fig. 2 **(a)** Transmission spectra of P0 (*black*) and P90 (*red*) tautomers. PDOS of **(b)** the molecule and **(c)** the NaCl upper layer. Contour plots of the LDOS on the **(d)** P0 and **(g)** P90 molecules at the Fermi energy along the molecular plane; **(e)** and **(h)**, along the molecular horizontal axis; **(f)** and **(i)**, along the molecular vertical axis, respectively. The molecular center locates on the Cl ion.

We then address the case where the molecular center sits on the Na ion. After relaxations, the planar geometry of the molecule was distorted, where the center was pushed upward from the molecular plane for both P0 and P90. The transmission spectra shown in Fig. 3(a) indicate that the P0 has higher transmission coefficients than the P90 has, as well as the conductance values of P0 ($1.70 \times 10^{-12} G_0$) and P90 ($1.05 \times 10^{-12} G_0$). However, P0 is energetically favored (by 0.07 eV). The PDOS of the NaCl upper layer in P0 junction is slightly higher than those in P90 one in the energy window between -0.012 eV and 0.012 eV. The PDOS on the molecule is similar for both P0 and P90. The contours of LDOS at E_f along molecular plane, along the molecular horizontal axis, and along the molecular vertical axis are shown in Figs. 3(d)–(i), respectively. No obvious LDOS difference is found between the P0 and P90 junctions, as the conductance difference is very small. The $\Gamma_{\mathrm{m-tip}}$ of P0 junction (6.05×10^{-8} eV) is larger than that of the P90 one (3.50×10^{-8} eV), agreeing with the conductance order.

Overall, the conductance of the molecule on the Cl ion is larger than that on the Na ion, while the molecule adsorbing on the latter site is about 0.4 eV [18] energetically favored. However, an accurate calculation of the molecular absorbed energy in this two probe (open) system should take the van der Waals interactions into account, which is still under constructing.

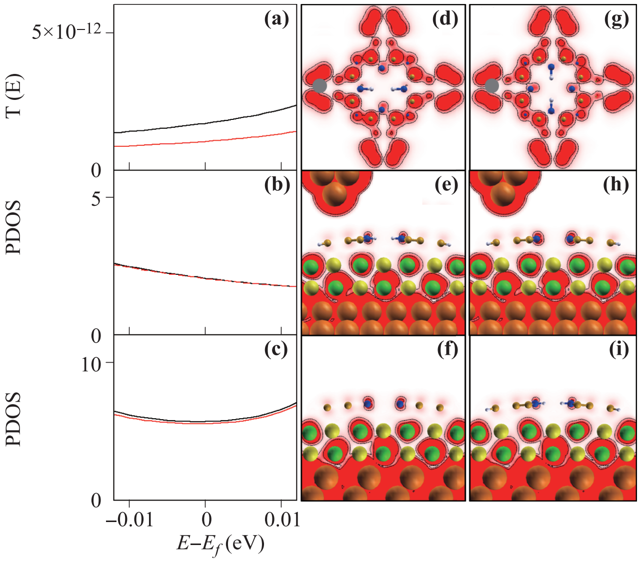

Fig. 3 **(a)** Transmission spectra of P0 (*black*) and P90 (*red*) tautomers. PDOS of **(b)** the molecule and **(c)** the NaCl upper layer. Contour plots of the LDOS on the **(d)** P0 and **(g)** P90 molecules at the Fermi energy along the molecular plane; **(e)** and **(h)**, along the molecular horizontal axis; **(f)** and **(i)**, along the molecular vertical axis, respectively. The molecular center locates on the Na ion.

4 Conclusions

We computationally investigate conductance switching properties of the double-barrier junction consisted of the phthalocyanine molecule adsorbed on a NaCl bilayer on an Au substrate and the tip. The hydrogen tautomerization in the phthalocyanine molecule results in distinct spatial extensions of the π orbitals and the two-level conductance. These orbitals hybridizing with the p_z orbitals of NaCl construct the transport channels of the junction. Changing the adsorbed site of molecule from the Cl ion to the Na ion can also switch the conductance values. Understanding charge transport at the atomic scale is of crucial importance for developing molecular electronics, giving us opportunities for designing advanced electronic devices.

Acknowledgements This work was partially supported by the Ministry of Science and Technology, Taiwan through No. 104-2112-M-001-008-MY3, and the National Center for Theoretical Sciences, Taiwan.

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