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Ambient Molecule Effects on the Electronic Transport of Pyrene-1,8-dithiol Molecular Junction

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Abstract. Due to the small size, single-molecule device may be sensitive to the ambient molecules. Thus, it is significant for fabricating single-molecule sensors to understand the influence of ambient molecule on molecular device. Based on the *ab initio* calculations combined with non-equilibrium Green's function method, the adsorption effects of H_2O, CO_2 and NO_2 molecule on the pyrene-1,8-dithiol molecular junctions are studied systematically. The numerical results show that, the influence of H_2O or CO_2 molecule on the pyrene-1,8-dithiol molecular junction is very slight when they are adsorbed on the pyrene-1,8-dithiol molecules, which attributes to the closed-shell ground states of these two molecules. Different from H_2O and CO_2 molecule, being a radical, NO_2 molecule shows obvious influence on the electronic transport of pyrene-1,8-dithiol molecular junctions. The system with NO_2 adsorbate is more conductive in the positive and lower negative bias regime than those of the other two molecular systems, which is due to the evident coupling between the states of NO_2 molecule and pyrene-1,8-dithiol molecule.

1. Introduction

Due to the rapid progress of single molecular technologies, great achievements have been obtained for single-molecule-device fabrications in recent years [1-15]. In the meantime, different strategies were developed to control and improve the functional properties of single-molecule device [16-18]. The effects of molecule-electrode interfaces [19-21], electrode distance [16,22], molecular anchor [23-25], side group [26-28], external field [29-31], external ambient [32,33], doping [18,34] and contamination [35-38] have been studied intensively. Attribute to the micro-dimension, the performance of single molecular device is easily affected by the external environment. The extent of the influence is not only related to the structure of the functional molecule, but also related to the surrounding molecule. It is important to understand the effects of surrounding molecule adsorption on the surface of functional molecule for which can provide the environmental information for building molecular devices [39]. According to the information one can know that: 1) which kind of functional molecule is more sensitive to the ambient molecule, and to which ambient molecule; 2) in what condition the performance of molecular devices can be unaffected or affected very slightly. Thus the optimal condition can be provided properly to build molecular device. Additionally, the molecular gas sensors can be also constructed by the corresponding study.

Since graphene is first discovered by Dr. Novoselov and Professor Geim in 2004 [39,40], the two-dimensional crystal have gained significant attention in condensed matter physics, chemistry, nanotechnology, and material science [39,41]. Particularly, graphene is an excellent adsorbent for its large specific surface area, rich pore structure and strong adsorption, which attracted many researchers to investigate the adsorption properties of graphene with gas molecule adsorbates extensively. Studies show that graphene is a potential material for gas sensors [36,37,39]. Pyrene can be seen as 2×2 graphene segment with the edge being saturated by H atoms. Therefore, pyrene may have some properties similar to the graphene, although the small size must result in obvious different characters from large surface graphene. Thus in this paper, the adsorption effects of the single H_2O, CO_2 and NO_2 molecule on pyrene molecule are studied systematically. In order to connect the functional molecule with gold electrodes, the S atoms are used to replace two H atoms at the two end of the pyrene molecule to form pyrene-1,8-dithiol molecule (denoted as PDT). Our studies show that, the H_2O and CO_2 adsorbate have slightly influence on the electronic transport of PDT molecular junction. However, the NO_2 adsorbate changes the current of PDT molecular junction with different extent in different bias regime.

2. Theoretical methods

In order to investigate the adsorption effects of H_2O, CO_2 and NO_2 molecules on the PDT molecular junctions, we sandwiched PDT molecule into the separation of two gold electrodes with H_2O, CO_2 or NO_2 molecule adsorbed on pyrene molecule backbone to form Au—PDT+$H_2O/CO_2/NO_2$—Au systems (see Figure. 2.1). The geometries of PDT molecular junctions with or without adsorbate molecules were optimized with a maximum force of 0.05 eV/Å in the Atomistix ToolKit (ATK) package. The Troullier–Martin type norm-conserving pseudopotentials are applied to represent the core electrons[42], the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) formulation is applied as the exchange-correlation functional[43,44]. For Au atoms, a single-ζ plus polarization basis set is used, and for other atoms, a double-ζ plus polarization basis set is employed. According to the Landauer– Buttiker formula[45], the current with different bias for the molecular junction is written as

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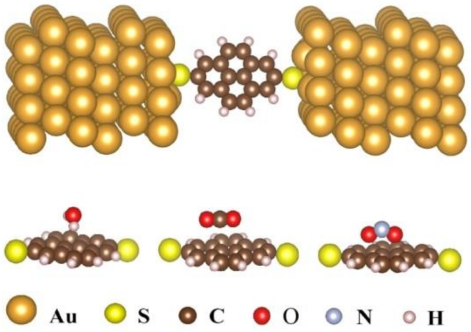

Figure 2.1: Schematic structures of PDT molecular junctions without or with $H_2O/CO_2/NO_2$ molecule adsorbed

$$I=\frac{2e}{h}\int T(E,V)[f(E-\mu_{\rm L})-f(E-\mu_{\rm R})]dE \qquad (1)$$

where, $T(E, V)$ is the transmission probability. μ_L and μ_R are the electrochemical potentials of the two electrodes. The transmission probability $T(E, V)$ is calculated by non-equilibrium Green's function (NEGF) method employing the ATK package. After current calculations, the differential conductance is obtained by $G=\partial I/\partial V$. A 5×5 k-point grid was used for the Brillouin-zone (BZ) sampling in the transverse directions.

3. Results and discussion

The geometric optimizations show that, the O atom of H_2O, the C atom of CO_2 and the N atom of NO_2 are all approximately sited on the top position of one central C atom of pyrene molecule with the perpendicular distances of about 0.36 nm, 0.31 nm and 0.34 nm, respectively. The geometries of the PDT molecules are changed very slightly with the effects of H_2O, CO_2 or NO_2 molecule adsorbate. The affinities for the three molecules adsorbed on the PDT molecules are 0.23 eV, 0.21 eV and 0.30 eV, respectively. One can see that the affinity of nonpolar CO_2 molecule is relatively weaker than those of the other two. While for the radical molecule NO_2 adsorbed on the PDT molecule, the affinity is obviously stronger than those of H_2O and CO_2 molecules adsorbed on the PDT molecules, which is due to the open-shell ground state of NO_2 molecule.

Figure 3.1 shows the currents and differential conductances of PDT molecular junction and the junctions with H2O, CO2 or NO2 adsorbate as functions of bias voltage. To our surprise, both the dipolar H2O molecule and nonpolar CO2 molecule adsorbed on the PDT molecules have little effects on the electronic transport of PDT molecular junction. Only the NO2 molecule has obvious influence on the electronic transport of the molecular junction. The peak conductance values appear at about ±1.0 V for the PDT molecular junctions with or without adsorbates. Figure 3.1(a) shows that the system with NO2 adsorbate is more conductive in the positive and lower negative bias regime than those of the other molecular systems. However, the differential conductance for the system with NO2 is decreased more rapidly when the positive bias is larger than 1.0 V. For the negative bias, the NO2 molecule only performs small effect on the current and differential conductance of the PDT molecular system.

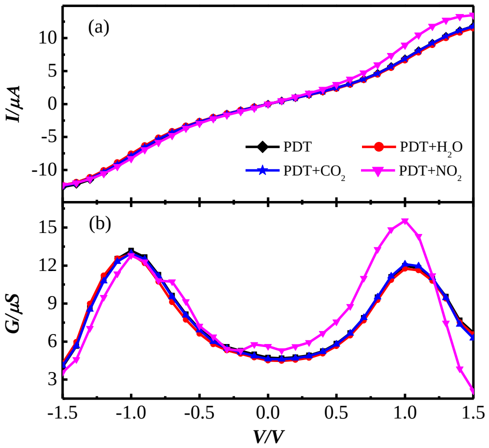

Figure 3.1: Electronic transport properties of PDT molecular junctions with H_2O, CO_2 and NO_2 molecule adsorbate. (a) Current and (b) Differential conductance as functions of applied bias voltage.

In order to understand why only NO_2 adsorbate has obvious effect on the electronic transport of PDT molecular junction, we present electronic transmissions of these four molecular junctions in Figure. 3.2. The figure shows that, for the bias of 0.0 V, the transmission shows a high and wide peak in the negative energy regime with a sharp transmission peak located on it. With the absolute value of the bias increasing, the height of the wide transmission peak decreases and slightly shifts to the high energy regime, however, the sharp transmission peak located at about -0.93 eV is slightly influenced by the change of bias voltage. The transmissions for the systems with H_2O and CO_2 molecules are almost unchanged in the bias windows. The main differences of transmissions for the system with H_2O and CO_2 molecules from the system without adsorbate are presented at about -1.0 eV, which

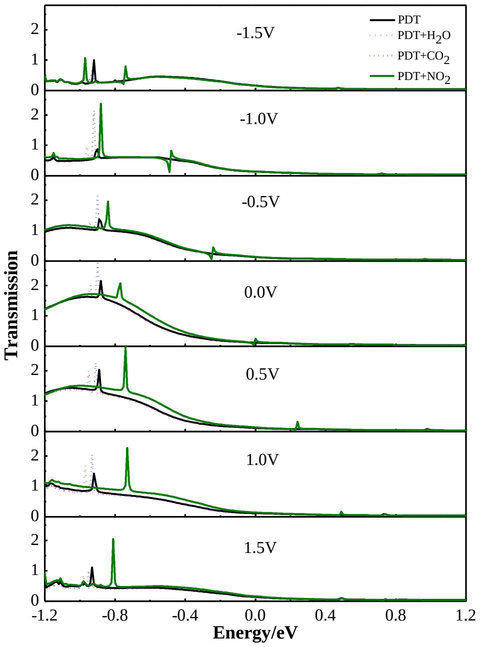

Figure 3.2: Transmission spectra of PDT molecular junctions without or with H_2O, CO_2 or NO_2 adsorbate

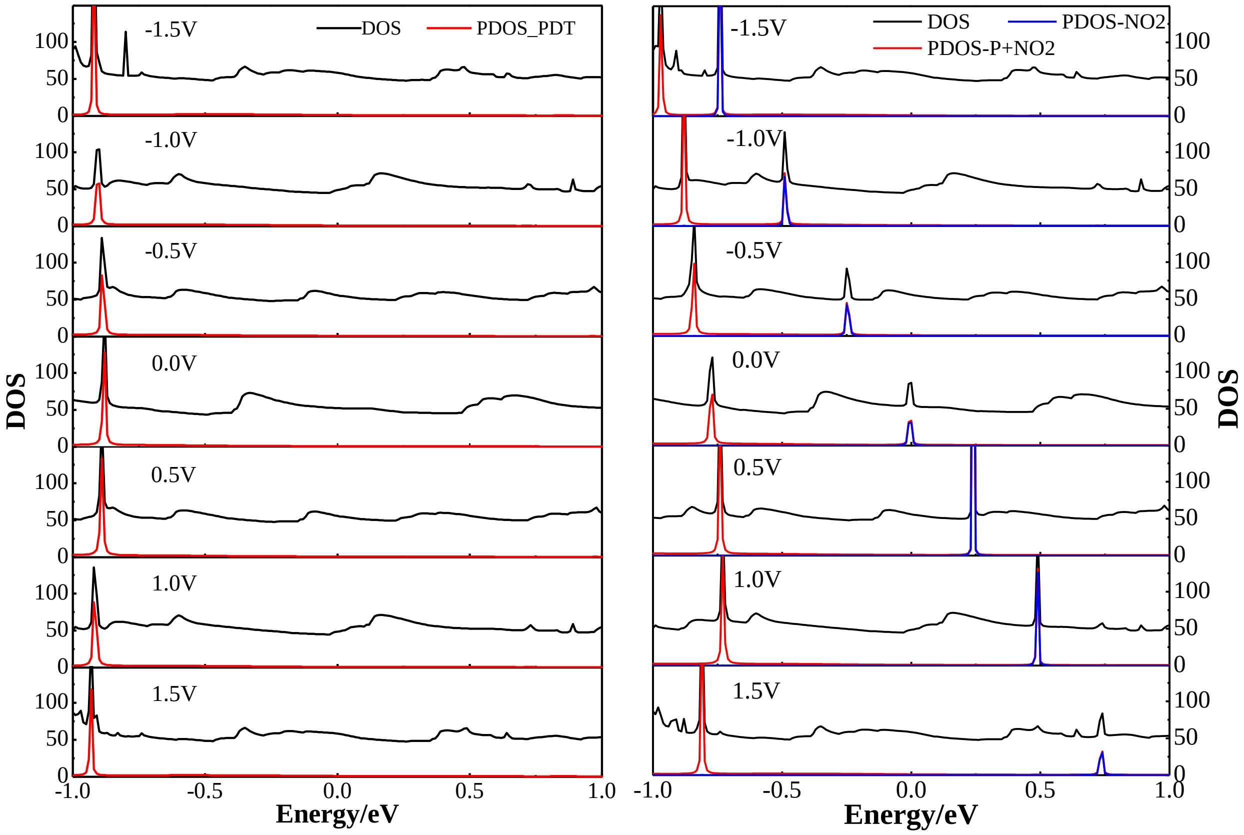

Figure 3.3: The DOSs of PDT molecular junctions without (left) or with (right) NO_2 adsorbate and the PDOSs of the PDT molecule (left), the NO_2 (right) and the PDT+NO_2 (right).

are obviously out of the bias windows. However, for the molecular junction with NO_2 molecule, there is a transmission peak in the bias window, which is shifted from -0.73 eV to 0.73 eV and gradually disappears with the bias being changed from -1.5 V to 1.5 V. Since the transmission peak is very small, and especially, the interference of energy level of NO_2 with the state of PDT molecular junction produces Fano resonance[46], this transmission peak resulted from NO_2 molecule only slightly influences the conductance of the molecular system. It is noticeable that, for the bias of 0.0 V, 0.5 V and 1.0 V, the transmissions of the system with NO_2 molecule from -1.0 eV to -0.2 eV are evidently higher than those of the systems without NO_2 adsorbate, which results in higher current and higher differential conductance of the system with NO_2 adsorbate.

Since the H2O and CO2 molecules perform little influence on the PDT molecular junctions, in the following we mainly discuss the NO2 adsorption effect on the PDT molecular system. Figure 3.3 shows the densities of states (DOSs) and the projected densities of states (PDOSs) for the PDT molecular system without or with NO2 adsorbate. The figure shows that, due to the eigenstates of PDT molecule being out of bias windows, the electronic transports mainly attribute to the contribution of electrode states which expanded into the pyrene regime. For the molecular system with NO2 molecule, although one energy level of NO2 molecule enters bias windows, it contributes very little to the electronic transport due to the localization of the state.

In order to gain deep insight into the electronic transports of the molecular systems, considering that the main contribution to the electronic transports attributing to the states of the electrodes expanded into the region that the PDT molecule locates, we presented spatial distributions of the molecular projected self-consistent Hamiltonian (MPSH) eigenstates of the system including the pyrene-1,8-dithiol without or with NO_2 adsorbate and the neighboring Au atoms for the bias voltages of 0.0 V, ±0.5 V, ±1.0 V and ±1.5 V in Figure. 3.4. The figure shows that, for the PDT molecular junction without NO_2 adsorbate, the lowest unoccupied molecular orbital (LUMO) is a localized orbital, which enters bias window only when the absolute value of the bias voltage is larger than 1.0 V. Thus it almost has no contribution to the electronic transport. Although the highest occupied orbital (HOMO) and HOMO-1 for the bias of 0.0 V and -0.5 V and the HOMO-1 for the bias of 0.5 V are well delocalized orbitals, they are all out of the bias windows. Thus they have little contribution to the electronic transports. However, for the bias of ±1.0 V, the HOMOs are well delocalized orbitals which are shifted into the bias windows and give evident contributions to the electronic transports, therefore the PDT molecular junction shows higher conductance at ±1.0 V than those at other bias voltages.

For the molecular junction with NO2 adsorbate, the LUMO is still a localized orbital, and has little contribution to the electronic transport. While the spatial distributions of the HOMO and the HOMO-1 show that the states of NO2 molecule are hybridized with the states of PDT molecular junctions. In detail, with the effects of NO2 molecule, the HOMO became more delocalized at negative bias, and the HOMO-1 became more delocalized at zero and positive bias. Especially, the HOMO-1 at 0.5 V and 1.0 V enhances

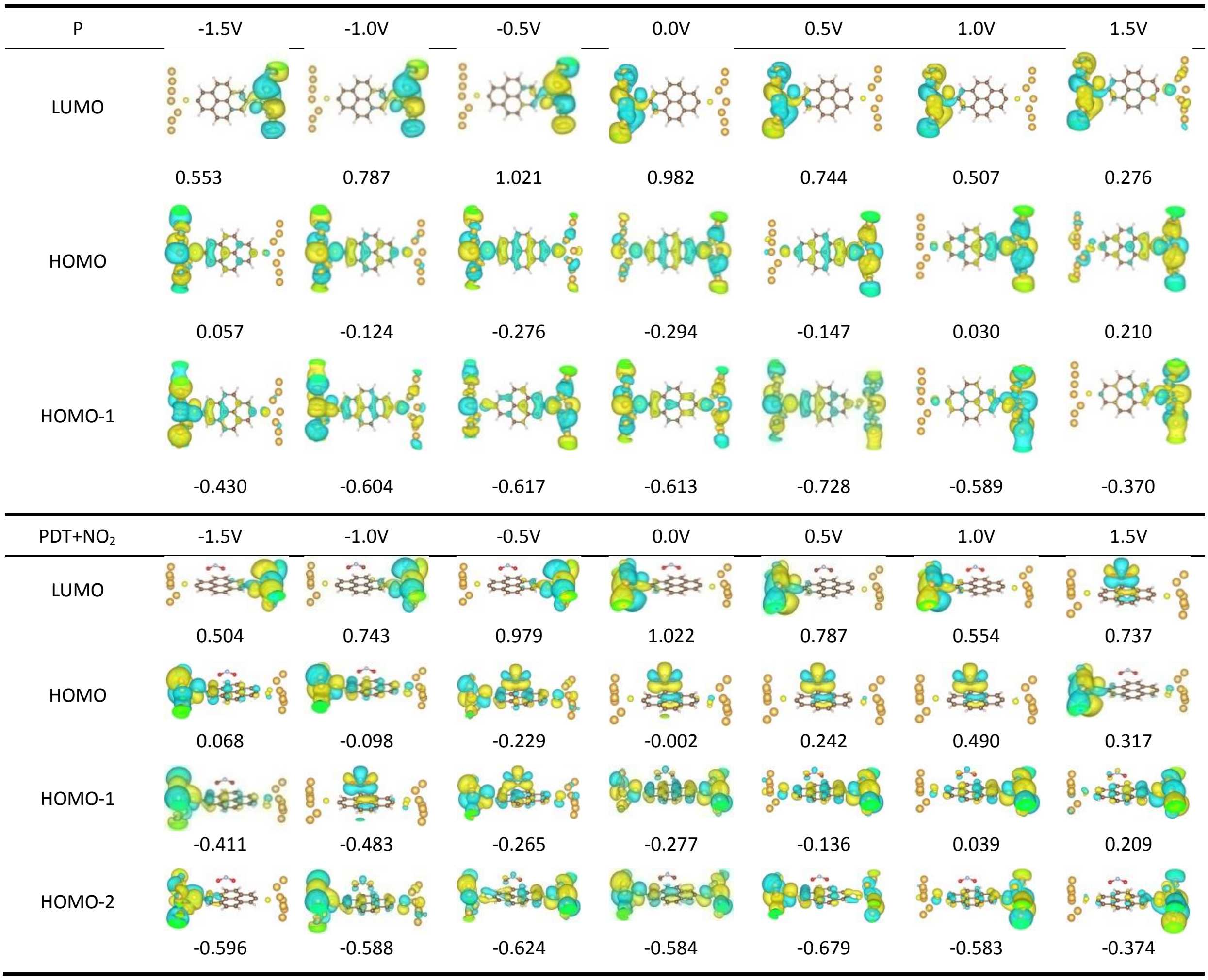

Figure 3.4: Molecular orbitals which have contributions to the electronic transports of PDT molecular junctions for the molecular junction without or with NO_2 adsorbate, where the corresponding orbital energy (unit: eV) of each orbital is also presented below each figure.

the transmission evidently, and consequently enhances the current of the PDT molecular system. Additionally, the HOMO-2 is also a delocalized molecular orbital. When the bias is larger than 1.0 V, the HOMO-2 gradually enters bias window and give non-negligible proportion of contribution to the electronic transport. Hence the PDT molecular junction with NO2 molecule adsorbate shows more conductive than the other molecular systems.

4. Conclusions

The ambient-molecule-adsorption effects on the electronic transport properties of PDT molecular junctions are studied by applying the density-functional theory and non-equilibrium Green's function method. The numerical results show that, the affinities for H2O, CO2 or NO2 molecule adsorbed on the PDT molecule are only 0.2-0.3 eV, which are typical physical adsorptions. Because the H2O and the CO2 molecule are closed-shell molecules, their eigenstates are generally out of bias windows in the lower bias regime. Therefore the H2O and the CO2 molecule have very weak influence on the electronic transport of PDT molecular junctions when they adsorbed on the PDT molecule. On the contrary, for the radical molecule NO2, its HOMO easily enters bias windows and couples with the states of the PDT molecule, which further induces obvious influence on the electronic transport of the molecular system.

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